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A SYSTEM OF INSTRUCTION  
IN  
QUALITATIVE CHEMICAL ANALYSIS

BY  
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LABORATORY IN THE COLLEGE OF PHARMACY OF THE  
CITY OF NEW YORK.

*THIRD EDITION.*  
REVISED AND ENLARGED.

LANE

1899  
—  
PUBLISHED BY THE AUTHORS  
117 CHAMBERS STREET  
NEW YORK CITY

A. S.

Entered, according to Act of Congress, in the year 1894,

BY

ARTHUR H. ELLIOTT, PH. D.,

And in the year 1899,

BY

ARTHUR H. ELLIOTT, PH. D.,

AND

GEORGE A. FERGUSON, PH. B.,

In the Office of the Librarian of Congress, at Washington, D. C.

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PRESS OF

GEO. GOTTSBERGER PECK

117 CHAMBERS ST., N. Y.

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1899

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## PREFACE TO FIRST EDITION.

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IN the preparation of this little manual, the first and main object sought to be attained, was to produce a handbook to be used with the living teacher. From an experience covering twenty years, a large part of which has been spent in the instruction of students in the laboratory, the author has found that chemical manipulation cannot be acquired by the reading of directions in a book alone.

Students that are given instruction by means of lectures and with such experimental demonstrations as are performed by the lecturer at that time, are usually incapable of repeating the experiments which they have seen when they are placed in a laboratory. Again, the lecturer giving the instruction does not have the opportunity to give the student that personal attention which the importance of the subject requires. It is usually some assistant who has to show the individual student those points that insure success in the work to be accomplished.

The results obtained by the author while instructing students in the laboratory and following the method given in these pages leads him to believe that the same will be found of service to others.

The author desires to acknowledge the kind help in the many suggestions received from Dr. Charles Rice, of Bellevue Hospital, New York.

ARTHUR H. ELLIOTT.

NEW YORK, October, 1892.

# 1. Introduction

The purpose of this paper is to study the properties of the function  $f(x)$  defined by the equation

$$f(x) = \int_0^x \frac{1}{1+t^2} dt$$

for  $x \in \mathbb{R}$ . We will show that  $f(x)$  is an odd function, i.e.,  $f(-x) = -f(x)$ , and that it is strictly increasing on  $\mathbb{R}$ . Furthermore, we will prove that  $f(x)$  is bounded on  $\mathbb{R}$  and that its range is  $(-\frac{\pi}{2}, \frac{\pi}{2})$ .

Let

2.

3.

4.

5.

6.

7.

## PREFACE TO THE THIRD EDITION.

---

THE second edition of this book has been exhausted and to supply the increased demand, the publication of a new edition has been rendered necessary.

In this new edition, although the original methods are adhered to, the field has been widened and the work made more useful by numerous additions, and in some instances by the substitution of schemes which have been found to be shorter and to give better results when used by the beginner in chemical analysis.

The scheme for the acids has been changed, a number of radicals being included which were not mentioned in the last edition. An endeavor is made to make this more practical for mixtures containing the interfering acid radicals. In the working out of these tests and separations, the authors wish to express their appreciation of the work done in this connection by Raymond J. Nestell and Russell H. Marsh, Ph.G.

As the work has been adopted as a text book in many institutions and as those engaged in teaching may not desire to use the new schemes, the authors have published in the last chapter those separations which were used in the preceding edition.

The authors trust that this new issue will meet with the same hearty welcome and appreciation as the former editions.

ARTHUR H. ELLIOTT, Ph.D.

GEORGE A. FERGUSON, Ph.B.

NEW YORK, September, 1899.



## INTRODUCTION.

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IT must be distinctly understood that the following pages are written for those who have a laboratory at their disposal and a teacher who is competent to show the manner of performing the more important experiments. With beginners it will be found necessary to proceed slowly at first in order to make them careful experimenters, and more patience is required at this point than would at first seem to be called for.

The course of instruction followed in these pages presupposes that the student has already a knowledge of the fundamental principles of chemistry, or is attending a course of instruction in the same, while he is working at the practical details of chemical analysis. This knowledge need not be very extensive for him to understand most problems in the writing of the more simple of the equations, and in a short time the difficult ones will prove interesting to him and he will work them out without assistance.

No attempt has been made to give instruction in chemical equations or in other theoretical questions. These are left to the judgment of the instructor to interpolate.

The method of making solutions of substances insoluble in water is explained after the student has become acquainted with the methods of analysis. At the beginning all solutions are prepared for him.

After a few operations involving precipitation, filtering and washing precipitates, it is best to take up the study of the metals. Many teachers prefer to start with the separation of the metals, while others consider a study of the special tests of each metal necessary before beginning the separations. In either case the student is shown each step of the manipulation, afterwards repeating the work himself. In this particular it is important to

5

note the care displayed in the use of reagents. The quantity of reagents used is a most important point to insist upon, and well repays the time spent in making the student repeat his work if he fails to imitate the instructor closely.

In order to limit the volume of fluid handled, and at the same time control the quantity of reagents used, all the operations must be performed in test-tubes, small dishes, etc.

Above all things the student should work with the instructor, and at exactly the same moment, upon the same materials and with a parallel set of apparatus, thus insuring success and giving a confidence inspired by no other method of working.

The method here described can be readily applied in classes of one hundred if the instructor is on a raised rostrum, where he can be easily seen by every member of the class, and where also he can note the progress of the individual student without difficulty, the rate of advance being determined by the progress of the reasonably bright members, and each step being explained as the work proceeds. Solutions of the metals are studied first; acids and salt radicals are taken up afterwards.

#### APPARATUS REQUIRED BY EACH STUDENT.

1. Ring-stand with ring, 2 inches inside diameter
- Bunsen burner
- Two feet of  $\frac{1}{4}$  inch rubber tubing
- Blowpipe tube for burner
- Blowpipe with fine tip
- Forceps of iron
- Three-inch steel spatula
- Triangular file, 6 inch
- Rat-tail file, 6 inch
- Pipe-stem triangle
- Charcoal from wood, not moulded
- Charcoal borer
- Platinum foil,  $2\frac{1}{2}$  by 1 inches
- Platinum wire three inches long, in glass holder
- Blue glass, 2 by 3 inches
- Mortar and pestle, 4 inch

Berlin evaporating dishes, 2 ½ and 3 inches

Funnels, 2 and 3 inches

Twelve test-tubes, 5/8 by 6 inches

Test-tube stand of wood

Test-tube brush

Two watch-crystals, 2 inch

Hydrogen sulphide generator

Wash-bottle with tubes, 16 oz.

Glass rods, 3 and 4 inches

Filter-papers, 3 and 4 inches

Advanced students may be supplied with the following apparatus in addition to the above :

Small beakers, 100 Cc.

Porcelain crucible, 1 inch

Crucible tongs

Platinum crucible

#### REAGENTS NEEDED BY EACH STUDENT.

2. These should be supplied to each student in bottles having glass stoppers, except the solution of Sodium Hydroxide, which should have a rubber stopper. The strength of each solution is given in the following list and is made with water unless otherwise stated. The strength of solutions means 1 gramme in cubic centimeters ; thus, 1 in 5 means 1 gramme in 5 cubic centimeters.

Hydrochloric Acid (concentrated)

Nitric Acid (concentrated)

Sulphuric Acid (concentrated)

Acetic Acid (50 per cent.)

Ammonium Chloride 1 in 5

Ammonium Hydroxide (1 of Aqua Aмм. Fort. and 2 of water)

Ammonium Sulphide; see 3

Ammonium Carbonate; see 4

Ammonium Oxalate 1 in 25

Sodium Hydroxide 1 in 5

Potassium Sulphocyanate 1 in 10



Disodium Orthophosphate 1 in 10  
 Magnesium Sulphate 1 in 10  
 Potassium Dichromate 1 in 20  
 Barium Chloride 1 in 10  
 Calcium Chloride 1 in 10  
 Calcium Hydroxide (Lime Water), saturated  
 Milk of Lime (Lime boiled several times with water to free  
     it from alkalies)  
 Potassium Iodide 1 in 20  
 Silver Nitrate 1 in 20  
 Potassium Ferrocyanide 1 in 10  
 Alcohol (ordinary)  
 Carbon Disulphide  
 Lead Acetate 1 in 10  
 Mercuric Chloride 1 in 20  
 Ferric Chloride: Liquor Ferri Chloridi U. S. P. 20 Cc.,  
     water 80 Cc.; or solid, 1 in 10  
 Ammonium Sulphate; see 5  
 Sodium Hypochlorite; see 7  
 Cupric Sulphate 1 in 10  
 Platinic Chloride 1 in 20  
 Molybdic Solution; see 6  
 Nessler's Solution; see 8

The following reagents are supplied to the student in wide-mouthed bottles:

Sodium Carbonate, anhydrous  
 Sodium Nitrate, powdered crystals  
 Borax, fused and powdered  
 Potassium Ferricyanide, crystals (dissolve as required;  
     solution decomposes)  
 Iron Sulphide, coarse powder  
 Ferrous Sulphate, crystals  
 Potassium Chlorate, crystals, small  
 Glycerin, concentrated  
 Starch  
 Copper wire, 1 inch pieces, and sheet zinc,  $\frac{1}{2}$  by  $\frac{1}{4}$  inch pieces  
 Litmus Paper, red and blue

3. *Ammonium Sulphide* should be made by saturating Ammonium Hydroxide (1 of Aqua Amm. Fort. and 2 of water) with Hydrogen Sulphide, and then adding an equal volume of the same Ammonium Hydroxide.

4. *Ammonium Carbonate* is made by taking

Ammonium Carbonate (clear lumps)..... 17 Gm.

Ammonium Hydroxide (1 Aqua Amm.

Fort., 5 water)..... 30 Cc.

Water.....to 100 Cc.

and shaking the mixture in a bottle until the lumps are dissolved.

5. *Ammonium Sulphate* is made by taking

Sulphuric Acid (concentrated)..... 10 Cc.

Water..... 40 Cc.

and adding excess of Ammonium Hydroxide to the mixture, or it may be made as needed.

6. *Molybdic Solution* is made as follows:

Take

Molybdic Acid..... 5 Gm.

Ammonium Hydroxide (1 of Aqua Amm.

Fort., 2 of water)..... 20 Cc.

Nitric Acid (1 of concentrated, 1 of water). 80 Cc.

Dissolve the Molybdic Acid in the Ammonium Hydroxide with gentle warming. Pour the solution thus obtained into the acid, carefully keeping the latter cool and adding the ammoniacal fluid very slowly and stirring all the time.

7. *Sodium Hypochlorite* is made as follows:

Take

Chlorinated Lime..... 10 Gm.

Water..... 100 Cc.

Sodium Carbonate Solution 1 in 5..... sufficient

Put the Chloride into a mortar and mix it by rubbing with the water. Transfer the mixture to a bottle, allow to stand and draw off with a syphon the solution from the insoluble matter. To this solution add the Sodium Carbonate solution slowly and with shaking, until on filtering a small portion of the mixture

no precipitate is obtained on adding a drop more Sodium Carbonate solution. Now allow the fluid to settle and draw off the clear solution for use.

8. *Nessler's Solution* is made as follows :

Take

Potassium Iodide.....	3.5 Gm.
Mercuric Chloride.....	1.6 "
Water.....	30 Cc.
Potassium Hydroxide (1 in 5).....	sufficient

Dissolve the Iodide in 10 c. c. of the water and the chloride in the balance, heating. Add the chloride solution to the iodide solution until a small precipitate is produced which does not disappear on stirring. Now add the Potassium Hydroxide solution until the mixture measures 100 c. c.

Allow to stand and pour off the clear fluid. To this clear fluid add more mercuric chloride solution until a small precipitate is obtained after stirring; allow to settle and this clear fluid is ready for use.

## CHAPTER I.

### SEPARATION OF THE METALS INTO GROUPS.

9. For the beginner it is only necessary to consider the more common of the metallic elements and the methods of separating them from one another. For this purpose the following metals *are assumed* to be in a single solution.

1	Pb. Lead (Plumbum)
	Hg <sub>2</sub> . Mercurous Mercury (Hydrargyrum)
	Ag. Silver (Argentum)
2	Hg. Mercuric Mercury
	Bi. Bismuth
	Cu. Copper (Cuprum)
	Cd. Cadmium
	As. Arsenic
	Sb. Antimony (Stibium)
3	Sn. Tin (Stannum)
	Co. Cobalt
	Ni. Nickel
	Fe. Iron (Ferrum)
	Mn. Manganese
	Cr. Chromium
	Al. Aluminium
4	Zn. Zinc
	Ba. Barium
	Sr. Strontium
	Ca. Calcium
	Mg. Magnesium
5	K. Potassium (Kalium)
	Na. Sodium (Natrium)
	NH <sub>4</sub> . Ammonium (hypothetical)

10. If to a solution *in a test-tube* containing all the above metals together hydrochloric acid is added in slight excess, only

the first three (or any one) will be precipitated. In other words, only these metals are capable of forming insoluble compounds with chlorine, the latter element leaving the hydrogen of the acid because it has a stronger affinity for the metals thrown out of solution. All the chlorides of these metals have a white color.

**11.** Before proceeding determine whether the quantity of hydrochloric acid has been sufficient to throw down all the Lead, Mercurous Mercury and Silver that may be in the solution. For this purpose the precipitated chlorides are allowed to settle, and a few drops more acid are added to the clear fluid above them. If this fails to produce any further precipitate the acid has done all that it will. If, on the other hand, it still causes a precipitate, continue adding the hydrochloric acid until it does not precipitate any more chlorides of the metals above mentioned.

**12.** This latter proceeding is termed "adding an excess" of the acid, and it is an extremely important step to learn in chemical analysis. If an insufficient amount of acid is added some of the metals will still remain in the solution, on the other hand, if too much acid is used, material is being added to the mixture that will interfere with the future work for the separation of the other metals.

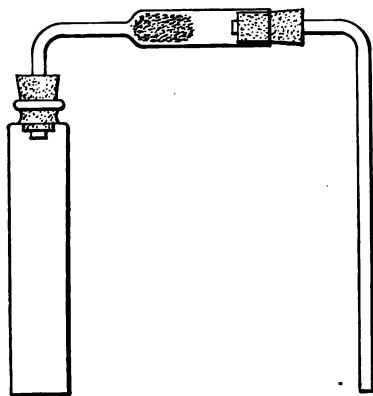
Having thus thrown down all the above mentioned metals in the manner described, decant off the fluid through a filter leaving the insoluble matter behind, and proceed with the filtrate as directed in the succeeding paragraphs. See also special tests for Bismuth and Antimony with hydrochloric acid.

The metals obtained above as chlorides may be called "the first group." The separation of the several metals from one another will be described later.

**13.** The filtrate from the first group of metals is now saturated with hydrogen sulphide gas. In order to do this the gas is allowed to bubble through this filtrate until it will take up no more of the same.

The apparatus shown in the annexed cut is found convenient for the generation of small quantities of hydrogen sulphide

as used in analysis. It consists of a long eight drachm vial with a small cork carrying a tube containing a little cotton. Into the larger end of this latter tube another cork is fitted to carry the finer tube delivering the gas. To use the apparatus place in the vial some coarsely broken iron sulphide and about one inch in depth of water; now add about fifteen drops of sulphuric acid, and give the gas a little time to start. In a few minutes a brisk effervescence takes place and the tube delivering the gas is put into the test-tube containing the solution to be saturated. If



the gas does not come off fast enough, after waiting a few minutes, add to the vial five or six drops more sulphuric acid, but do not add the acid in too large quantities, as the gas may come off so fast as to be unmanageable, and the fluid in the vial may flow over into the solution being saturated. The apparatus is sufficiently simple to be readily constructed by the student, as instead of the en-

larged tube carrying the cotton a tube having a cork in each end may be used for the purpose.

A good way to ascertain when the filtrate is saturated is to remove the tube delivering the gas and shake the test tube with the opening tightly closed with the thumb. If there is a pressure on the thumb when the test tube is shaken, the filtrate is saturated with gas; if, on the other hand, there is a suction on the thumb, the gas must be passed through the solution again.

**14.** The sulphur of the hydrogen sulphide unites with the metals Mercuric Mercury, Bismuth, Copper, Cadmium, Arsenic, Antimony, and Tin, to form insoluble sulphides with them. These compounds are only completely precipitated when the filtrate from the first group is perfectly saturated with hydrogen sulphide gas. These sulphides are from the "second group"

of metals. In color the sulphides of Mercury, Bismuth and Copper are black; Tin is brown or yellow; Arsenic and Cadmium are yellow; Antimony is orange. These sulphides are filtered from the solution and the precipitate is set aside for future use. To insure the complete precipitation of the metals of this group, pass more of the gas through the filtrate. If no more precipitate is obtained the group has been entirely separated; if, on the other hand, a precipitate is obtained, this is filtered off on the same paper previously used.

**15.** To the filtrate last obtained now add some ammonium chloride solution equal to about  $\frac{1}{4}$  of the volume of the fluid in the test tube. To the same fluid add enough ammonium hydroxide to give it an odor of the latter after shaking. Finally add to the same mixture some ammonium sulphide.

**16.** The addition of the ammonium hydroxide may produce a precipitate but this is disregarded for the time being. The ammonium sulphide gives up its sulphur to the metals Cobalt, Nickel, Iron, Manganese and Zinc, while Aluminium and Chromium are precipitated as hydroxides. In color, the sulphides of nickel, cobalt and iron are black, manganese dirty pink, zinc white, chromium hydroxide pale green, and aluminium hydroxide white.

In order to ascertain if enough sulphide has been added, the solution must be filtered, and a few drops more of the ammonium sulphide mixed with the clear filtrate. If the sulphide has not been added in sufficient quantity, this second addition will produce more precipitate which must be filtered out, and the clear filtrate treated again with the reagent. When enough has been added, the further addition will give no precipitate. Here, again, care must be taken that "an excess" of the precipitant is used, before going on to the next step in the analysis.

The mixture of sulphides and hydroxides obtained in the last case is from the "third group" of metals.

**17.** The filtrate from the group last obtained is mixed with ammonium carbonate solution, and thoroughly shaken and then warmed. Here also the same precaution must be taken to in-

sure "an excess" of the carbonate, as was followed in the case of ammonium sulphide.

**18.** The precipitate obtained may contain the metals Barium, Strontium and Calcium as carbonates. These metals unite with the carbonic acid radical of the ammonium carbonate to form insoluble compounds in the presence of the ammonium hydroxide. All these carbonates are white.

The precipitate so obtained is from the "fourth group" of metals.

**19.** In the filtrate from the ammonium carbonate precipitate there may be present in combination the metals Magnesium, Potassium and Sodium ; together with Ammonium Salts.

The last filtrate obtained gives what is termed the "fifth group" of metals.

**20.** Since ammonium salts have been added to effect the separation of the first four groups of metals, the test for ammonium in the filtrate last obtained cannot be made. A special test for ammonium is applied to the original solution before any reagents have been added to it.

The various operations described above may be tabulated in the following form:



## GROUP TABLE

To the clear solution add HCl in slight excess. Filter and wash.

<b>Ppt.*</b> —Treat as per Table I. Contains Pb, Hg, and Ag as Chlorides.	<b>Filtrate.</b> —Warm and pass H <sub>2</sub> S gas until thoroughly saturated. Filter and wash.
<b>Ppt.</b> —Treat as per Table II. Contains Pb, Hg, Bi, Cu, Cd, As, Sb and Sn as Sulphides.	<b>Filtrate.</b> —Add NH <sub>4</sub> Cl ( $\frac{1}{4}$ vol) then NH <sub>4</sub> OH in excess, and then (NH <sub>4</sub> ) <sub>2</sub> S in slight excess. Shake well. Filter and wash.
<b>Ppt.</b> —Treat as per Table III. Contains Co, Ni, Fe, Mn, and Zn as Sulphides, with Cr and Al as Hydroxides.	<b>Filtrate.</b> —Add (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> in slight excess. Warm. Filter and wash.
<b>Ppt.</b> —Treat as per Table IV. Contains Ba, Sr and Ca as Carbonates.	<b>Filtrate.</b> —Treat as per Table V. Contains Mg, K, Na, and NH <sub>4</sub> salts together with the reagents added.

\*Abbreviation for Precipitate.

## CHAPTER II.

---

### SPECIAL TESTS FOR THE METALS OF THE FIRST GROUP.

---

#### LEAD.

##### *Blowpipe Test.*

**21.** Heated on charcoal with sodium carbonate, malleable metallic globules are obtained.

##### *Solution Tests.*

**22.** Hydrochloric acid and soluble chlorides give white precipitates of lead chloride,  $\text{PbCl}_2$ . In dilute solutions this precipitate does not form. Precipitate is soluble in 135 parts of cold water and 30 parts of hot water, also in alkali acetates and thiosulphates. Insoluble in strong alcohol.

**23.** Potassium iodide and soluble iodides give yellow precipitates of lead iodide,  $\text{PbI}_2$ . Soluble in 2000 parts of cold and 149 parts of hot water. By cooling the hot water solution, the dissolved salt separates out as brilliant yellow spangles. Also soluble in fixed alkalies, potassium iodide, sodium thiosulphate, and in a hot solution of ammonium chloride.

**24.** Hydrogen sulphide and soluble sulphides give a black precipitate of lead sulphide,  $\text{PbS}$ . If much hydrochloric acid is present the color may be red and the precipitate consists of lead chloride and lead sulphide. This precipitate is decomposed by hot nitric acid, forming nitrate or sulphate, or both, according to the strength of acid used. It is insoluble in cold dilute acids, alkaline hydroxides and sulphides, and potassium cyanide.

**25.** Alkaline hydroxides ( $\text{K}$ ,  $\text{Na}$ ,  $\text{NH}_4$ ), give white precipitates of lead hydroxide mixed with basic salt. Soluble in excess

of the first two, insoluble in excess of the last. Soluble in dilute nitric acid. In the case of lead acetate, ammonium hydroxide does not give an immediate precipitate.

**26.** Sodium carbonate and soluble carbonates give white precipitates of basic carbonate,  $2\text{PbCO}_3$ ,  $\text{Pb}(\text{OH})_2$ , more or less soluble in excess. Soluble to a very slight extent in water, solubility increased by ammonium salts and carbon dioxide. Insoluble in potassium cyanide.

**27.** Potassium chromate and soluble chromates and dichromates give yellow precipitates of lead chromate,  $\text{PbCrO}_4$ . Soluble in potassium hydroxide and hydrochloric acid. Insoluble in acetic acid and dilute nitric acid.

**28.** Sulphuric acid and soluble sulphates give fine white precipitates of lead sulphate,  $\text{PbSO}_4$ . Dilute solutions do not give an immediate precipitate, precipitation facilitated by alcohol. Soluble to a slight extent in strong nitric and hydrochloric acids, more soluble in potassium hydroxide and ammonium salts, especially the acetate. Insoluble in dilute acids.

**29.** Potassium ferrocyanide gives a white precipitate of lead ferrocyanide.

**30. Commercial Lead Compounds :**

**Alloys :**

Shot —(Lead with 40 lbs. of arsenic to the ton.)

Solder—Lead and tin.

Type metal—Lead and antimony.

**Oxides and Salts :**

Litharge—Lead Oxide,  $\text{PbO}$ .

Red Lead—Minium,  $\text{Pb}_3\text{O}_4(2\text{PbO}, \text{PbO}_2)$ .

Chrome Yellow—Lead Chromate,  $\text{PbCrO}_4$ .

White Lead—Basic Lead Carbonate  $2\text{PbCO}_3$ ,  $\text{Pb}(\text{OH})_2$ .

Sugar of Lead, Lead Acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , soluble 1 in 1.5 of water.

Goulard's Solution—Basic Lead Acetate,  $\text{PbO}(\text{C}_2\text{H}_3\text{O}_2)_2$ , (Solution-25%).

Puce Lead Oxide—Lead Dioxide,  $\text{PbO}_2$ .

Lead Iodide  $\text{PbI}_2$ .

" Nitrate,  $\text{Pb}(\text{NO}_3)_2$ , soluble 1 in 2 of water.

### MERCUROUS COMPOUNDS.

#### *Blowpipe Tests.*

**31.** Volatilized by heating.

Heated in tube with dry sodium carbonate, fine globules of the metal are obtained.

#### *Solution Tests.*

**32.** Hydrochloric acid and soluble chlorides give white precipitates of mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ . Soluble in aqua regia and chlorine water. Insoluble in cold dilute acids. Decomposed by potassium, sodium, and ammonium hydroxides; the first two giving black mercurous oxide,  $\text{Hg}_2\text{O}$ ; the last, black amido-mercurous chloride,  $\text{NH}_2\text{Hg}_2\text{Cl}$ .

**33.** Potassium iodide and soluble iodides give green to yellow precipitates of mercurous iodide,  $\text{Hg}_2\text{I}_2$ . Slightly soluble in water. In contact with a solution of potassium iodide, the salt is decomposed into mercuric iodide, which dissolves, leaving a residue of metallic mercury.

**34.** Hydrogen sulphide and soluble sulphides give black precipitates of mercuric sulphide with mercury,  $\text{HgS.Hg}$ . Soluble in aqua regia, sodium sulphide and hydrosulphide; sodium sulphide leaving a residue of mercury. Insoluble in dilute acids, ammonium sulphide, and potassium cyanide.

**35.** Sodium and potassium hydroxides give black precipitates of mercurous oxide,  $\text{Hg}_2\text{O}$ ; insoluble in excess of the reagents. Soluble in nitric acid.

**36.** Ammonium hydroxide gives a black precipitate of an amido-mercurous compound; insoluble in excess of the reagent.

**37.** Copper wire takes a coating of metallic mercury.

**38.** Potassium dichromate gives a red precipitate. Soluble in nitric acid.

**39.** Stannous chloride gives a white precipitate of mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ , changing to black metallic mercury.

For commercial compounds see mercuric compounds, paragraph 64.

## SILVER.

### *Blowpipe Test.*

**40.** On charcoal with sodium carbonate gives bright white metallic globules.

### *Solution Tests.*

**41.** Hydrochloric acid and soluble chlorides give white, curdy precipitates of silver chloride,  $\text{AgCl}$ , becoming dark in color on exposure to sunlight. Soluble in ammonium hydroxide and reprecipitated by excess of nitric acid; also in strong hydrochloric acid and concentrated solutions of alkaline chlorides, reprecipitated by diluting with water. Insoluble in nitric acid.

**42.** Potassium iodide and soluble iodides give yellow precipitates of silver iodide,  $\text{AgI}$ . Soluble in a large excess of ammonium hydroxide, in potassium cyanide, and in a concentrated solution of potassium iodide. Insoluble in water, alcohol and dilute acids.

**43.** Hydrogen sulphide and soluble sulphides give black precipitates of silver sulphide,  $\text{Ag}_2\text{S}$ . Soluble in boiling nitric acid, and in potassium cyanide. Insoluble in dilute acids, alkali hydroxides and sulphides.

**44.** Sodium and potassium hydroxides give gray-brown precipitates of silver oxide,  $\text{Ag}_2\text{O}$ ; insoluble in excess of the reagents. Soluble in ammonium hydroxide.

**45.** Ammonium hydroxide in small quantity gives the same precipitate as the previous test, soluble in excess of the reagent.

**46.** Potassium dichromate gives a dark red precipitate of silver chromate,  $\text{Ag}_2\text{CrO}_4$ . Soluble in nitric acid and ammonium hydroxide. In slightly acid solutions, silver dichromate,  $\text{Ag}_2\text{Cr}_2\text{O}_7$  forms.

### **47. Commercial Silver Compounds:**

Alloy:

Silver coin—silver and copper.

**Oxides and salts:**

**Silver oxide—** $\text{Ag}_2\text{O}$ .

**Silver nitrate—** $\text{AgNO}_3$ , soluble 1 in 0.6 parts of water ; 1 in 26 parts of alcohol.

**Lunar caustic—**fused silver nitrate.

**Silver cyanide—** $\text{AgCN}$ .

**Silver iodide—** $\text{AgI}$ . Used in pharmacy and photography.

“ **bromide—** $\text{AgBr}$ . Used in photographic dry plates.



## CHAPTER III.

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### SEPARATION OF THE METALS OF THE FIRST GROUP.

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The group precipitate obtained by adding hydrochloric acid in excess and filtering, should always be washed with water to free it from the fluid that adheres to it and which contains some of the metals of the other groups, as well as the reagent used for precipitating the group.

**48.** The first step, then, is to wash with cold water. For this purpose use the jet of the wash bottle, throwing the stream around the edges of the filter paper in a uniform manner. Always let the first lot of water pass through the funnel before adding a second quantity. Two washings, filling the funnel half full each time, will be sufficient.

**49.** Do not add the wash water to the filtrate but allow it to run into another vessel. It may be thrown away unless it is needed to dilute the filtrate to a convenient volume.

**50.** Transfer the precipitate to a test tube by making a hole in the lower part of the filter paper and washing the precipitate off with water from the wash bottle. Boil the mixture in the test tube for a short time, care being taken not to heat the tube directly on the bottom.

**51.** After the first boiling, allow the precipitate to settle and pour off the hot fluid into another tube through a filter paper, setting the fluid aside for future use. Add more water to the precipitate and boil again. This second hot fluid may be thrown away; it serves to dissolve out any of the soluble compound possibly left after the first treatment.

**52.** The first hot water solution is now tested for lead. For this purpose the fluid is cooled and divided into two parts. To



one portion a few drops of potassium dichromate are added, a yellow precipitate proves the presence of *lead*. To the second portion a few drops of sulphuric acid and a few drops of alcohol are added, a white precipitate proves the presence of *lead*.

**53.** Now return to the precipitate insoluble in boiling water. To this add ammonium hydroxide in sufficient quantity to fill the test tube about one-quarter full. The mixture should be thoroughly shaken and then filtered.

**54.** If the precipitate on the filter paper is black, *mercury(ous)* is present. To confirm this, wash the precipitate with water, remove with a spatula, and dissolve in a few drops of aqua regia, heat to expel the excess of acid used, dilute with three or four volumes of water, and then add stannous chloride; a white precipitate changing to grayish-black proves the presence of mercury.

**55.** To the filtrate from the black precipitate add nitric acid, shaking well between each addition until the fluid turns blue litmus paper to red. A white precipitate proves the presence of *silver*.

The reasons for the steps taken in this separation are as follows:

**56.** The group precipitate consists of the chlorides of lead, mercurous mercury, and silver. Lead chloride is soluble in hot water and is removed from the other two, which are insoluble in this fluid, by boiling. Potassium dichromate and sulphuric acid produce salts of lead which are insoluble in both hot and cold water. The addition of ammonium hydroxide to the precipitate remaining after the treatment with hot water, decomposes the mercurous chloride, and a black, amido-mercurous chloride is formed. At the same time the silver chloride is dissolved. By neutralizing the ammonium hydroxide solution by means of an acid, the white silver chloride is again precipitated.

TABLE I. HCl Group.

Boil the Ppt. with water, allow to settle, pour off liquid into another tube, and repeat the boiling with water. Reserve insoluble and filter the fluids hot.

<p><b>Filtrate.</b>—To part of fluid add a few drops of <math>H_2SO_4</math> and alcohol. A white ppt. is <math>PbSO_4</math> and indicates <b>Pb</b>.</p>	<p><b>Insoluble.</b>—Add <math>NH_4OH</math>, shake well and filter.</p>	<p><b>Insoluble.</b>—Is black, and is <math>NH_2Hg_2Cl</math>. Indicates <b>Hg</b>.</p>	<p><b>Filtrate.</b>—Add <math>HNO_3</math> in slight excess. A white milky ppt. is <math>AgCl</math> and indicates <b>Ag</b>.</p>	<p>25</p>
<p>To another portion add a few drops of <math>K_2Cr_2O_7</math>. A yellow ppt. is <math>PbCrO_4</math> and indicates <b>Pb</b>.</p>				<p>25</p>



## CHAPTER IV.

### SPECIAL TESTS FOR THE METALS OF THE SECOND GROUP.

#### MERCURIC COMPOUNDS.

##### *Blowpipe Tests.*

**57.** Same as mercurous compounds.

##### *Solution Tests.*

**58.** Hydrogen sulphide and soluble sulphides give black precipitates of mercuric sulphide,  $\text{HgS}$ . If reagent is added in small quantities, the precipitate is first white, then yellow, orange and red, and finally black. Soluble in aqua regia, hot hydrochloric acid, potassium and sodium sulphides mixed with hydroxides. Almost insoluble in ammonium sulphide, especially the yellow solution. Insoluble in potassium hydroxide and cyanide, nitric acid, and hydrosulphides.

**59.** Potassium iodide and soluble iodides give scarlet precipitates of mercuric iodide,  $\text{HgI}_2$ . Soluble in excess of the precipitant used and also in mercuric chloride and sodium thiosulphate. Decomposed by strong hot nitric acid, liberating iodine.

**60.** Potassium and sodium hydroxides give precipitates of mercuric oxide (yellow),  $\text{HgO}$ . With small quantities of hydroxide the precipitate is red-brown and contains basic salt. Excess of the hydroxide finally gives mercuric oxide. Insoluble in excess of the hydroxide. Soluble in dilute hydrochloric and nitric acids. Decomposed when dry by heat into mercury and oxygen.

**61.** Ammonium hydroxide gives a precipitate of white amido-mercuric compounds. With mercuric chloride the precipitate is amido-mercuric chloride,  $\text{NH}_2\text{HgCl}$ . Insoluble in excess of

the hydroxide. Soluble in hydrochloric, nitric and acetic acids ; in ammonium carbonate, and sodium thiosulphate.

**62.** Copper wire, same as mercurous compounds.

**63.** Stannous chloride, same as mercurous compounds.

**64.** *Commercial Mercury Compounds :*

Alloys: (Amalgams).

Mirror amalgam—mercury and tin.

Electric “ —mercury, zinc and tin.

Gold “ (dental)—mercury and gold.

Cadmium “ ( “ )—mercury and cadmium.

Oxides and Salts :

Red precipitate—mercuric oxide  $\text{HgO}$ .

Black wash—mercurous oxide  $\text{Hg}_2\text{O}$  (calomel and lime water).

Calomel—mercurous chloride  $\text{Hg}_2\text{Cl}_2$ .

Corrosive sublimate—mercuric chloride  $\text{HgCl}_2$ , soluble 1 in 16 of water ; 1 in 3 of alcohol.

Yellow or green iodide of mercury—mercurous iodide  $\text{Hg}_2\text{I}_2$

Red iodide of mercury—mercuric iodide  $\text{HgI}_2$ .

Fusible white precipitate—diammonium mercuric chloride  $(\text{NH}_3)_2\text{HgCl}_2$ .

Infusible white precipitate—amido-mercuric chloride  $\text{NH}_2\text{HgCl}$ .

Vermilion—mercuric sulphide  $\text{HgS}$ .

## BISMUTH.

### *Blowpipe Tests.*

**65.** Heated on charcoal with sodium carbonate, in the reducing flame gives brittle metallic particles.

**66.** Heated with a mixture of sulphur and potassium iodide gives a scarlet coat.

### *Solution Tests.*

**67.** Hydrochloric acid and soluble chlorides give white precipitates of bismuth oxychloride,  $\text{BiOCl}$ , if there is not too much free acid present. Soluble in strong acids. Insoluble in water.

**68.** Hydrogen sulphide and soluble sulphides give brownish-black precipitates of bismuth sulphide,  $\text{Bi}_2\text{S}_3$ . Soluble in strong nitric acid. Insoluble in dilute acids, in alkalies, alkali sulphides, and potassium cyanide.

**69.** Alkali hydroxides ( $\text{K}, \text{Na}, \text{NH}_4$ ) give white precipitates of basic bismuth hydroxide,  $\text{BiOOH}$ . Insoluble in excess of the precipitants. Soluble in hydrochloric, nitric, and sulphuric acids.

**70.** Sodium carbonate and soluble carbonates give white precipitates of basic bismuth carbonate  $\text{Bi}_2\text{O}_2\text{CO}_3$ . Insoluble in excess of the precipitant and in potassium cyanide. Soluble in hydrochloric and nitric acids.

**71.** Potassium chromate and soluble chromates and dichromates give yellow precipitates of bismuth chromate,  $\text{Bi}_2(\text{CrO}_4)_3$ . Soluble in dilute nitric acid. Insoluble in potassium and sodium hydroxides.

**72.** Water precipitates basic salts.

**73.** Cinchonine nitrate with potassium iodide gives a dark-red precipitate.

**74. Commercial Bismuth Compounds :**

Alloys :

Wood's alloy for dentists. Bi 4, Pb 2, Sn 1, Cd 1.

Type metal sometimes contains 2 per cent. of Bi.

Oxides and Salts :

Bismuth cream,  $\text{BiO}_3\text{H}_3$ , 20 parts in 100 of water.

Bismuth subcarbonate,  $\text{Bi}_2\text{O}_2\text{CO}_3, \text{H}_2\text{O}$ .  
Bismuth subnitrate,  $\text{BiONO}_3, \text{H}_2\text{O}$ . } Formulæ are un-  
certain.

Bismuth citrate,  $\text{BiC}_6\text{H}_5\text{O}_7$ .

Flake white is bismuth subnitrate.

Pearl white is bismuth oxychloride.

**COPPER.**

*Blowpipe Tests.*

**75.** Heated in the reducing flame gives red metallic globules.

**76.** On platinum wire in flame, gives emerald green or azure-blue color, according to compound tested.

**77.** Borax bead, in oxidizing flame, green hot, blue or greenish-blue cold; in reducing flame, greenish or colorless hot, opaque and brownish-red cold.

*Solution Tests.*

**78.** Hydrogen sulphide and soluble sulphides give brown-black precipitates of copper sulphide,  $\text{CuS}$ . Soluble in hot nitric acid and in potassium cyanide. Slightly soluble in ammonium sulphide. Insoluble in dilute acids, sodium and potassium sulphides, and alkali hydroxides.

**79.** Sodium and potassium hydroxides give light blue precipitates of copper hydroxide,  $\text{Cu(OH)}_2$ , converted by boiling into black copper oxide,  $\text{CuO}$ . Precipitation prevented by presence of organic acids. Soluble in hydrochloric, nitric, and sulphuric acids.

**80.** Ammonium hydroxide in small quantity gives a light blue precipitate of copper hydroxide. Soluble in excess of the reagent forming a blue solution.

**81.** Sodium and potassium carbonates give greenish-blue precipitates of basic copper carbonate,  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ . Soluble in ammonium hydroxide and potassium cyanide, hydrochloric and nitric acids.

**82.** Ammonium carbonate acts like ammonium hydroxide.

**83.** Potassium ferrocyanide gives a reddish-brown precipitate of copper ferrocyanide,  $\text{Cu}_2\text{Fe(CN)}_6$ . Insoluble in dilute acids and decomposed by alkaline hydroxides. In very dilute solutions only a red color is produced.

**84.** *Commercial Copper Compounds:*

*Alloys:*

Brass—copper and zinc.

Bronze—copper, tin and zinc.

Bell Metal—copper and tin.

Speculum Metal—copper and tin.

German Silver—copper, zinc, nickel.

Aluminium Bronze—copper with 10% Al.

### Oxides and Salts:

Black Oxide— $\text{CuO}$ , Cupric Oxide.

Red Oxide— $\text{Cu}_2\text{O}$ , Copper Scale. Suboxide. Cuprous Oxide.

Blue Vitriol— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Cupric Sulphate. Blue-stone. Soluble 1 in 2.6 of water.

Scheele's Green—Cupric Arsenite,  $\text{CuHAsO}_3$ .

Paris Green—Aceto-arsenite of copper. Composition variable.

Verdigris—Basic Cupric Acetate. Composition variable.

Copper Acetate— $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$ . Soluble 1 in 15 of water; 1 in 135 of alcohol.

### CADMIUM.

#### *Solution Tests.*

85. Hydrogen sulphide and soluble sulphides give bright yellow precipitates of cadmium sulphide,  $\text{CdS}$ . Precipitation prevented by presence of much free acid. Soluble in hot nitric acid; hot hydrochloric acid; and hot, dilute sulphuric acid. Insoluble in cold, dilute acids; in alkali hydroxides and sulphides; and potassium cyanide.

86. Sodium and potassium hydroxides give white precipitates of cadmium hydroxide,  $\text{Cd}(\text{OH})_2$ . Insoluble in excess. Soluble in hydrochloric, nitric, and sulphuric acids.

87. Ammonium hydroxide gives a white precipitate of cadmium hydroxide. Soluble in excess. Reprecipitated by diluting and by potassium and sodium hydroxides.

88. Alkaline carbonates,  $(\text{Na}, \text{K}, \text{NH}_4)$  give white precipitates of cadmium carbonate,  $\text{CdCO}_3$ . Insoluble in excess of the first two, slightly soluble in excess of the last. Soluble in potassium cyanide and in hydrochloric, nitric, and sulphuric acids. Precipitation retarded by ammonium salts and prevented by ammonium hydroxide.

#### 89. *Commercial Cadmium Compounds:*

##### Alloys:

Fusible alloy—bismuth, lead, tin and cadmium.



Wood's alloy—see Bismuth alloys.

**Oxides and Salts:**

Cadmium yellow— $\text{CdS}$ , cadmium sulphide. An artist's pigment.

Cadmia—same as preceding. Some varieties contain thallium.

**ARSENIC.**

*Blowpipe Tests.*

**90.** Heated on charcoal with sodium carbonate gives an odor of garlic and a white volatile coat.

**91.** Heated in a closed glass tube with potassium cyanide and sodium carbonate (1 and 3) gives a black mirror of arsenic. On opening the closed end of the tube and heating the mirror, a white deposit is formed in the upper part of the tube.

**92.** Heated in a glass tube in the upper part of which is some red-hot charcoal, a black mirror of arsenic is formed above the charcoal.

*Solution Tests.*

**ARSENIOUS COMPOUNDS.**

**93.** Hydrogen sulphide and soluble sulphides in acid solutions give yellow precipitates of arsenious sulphide,  $\text{As}_2\text{S}_3$ . Soluble in alkali sulphides, hydroxides, carbonates and bicarbonates; from which solutions hydrochloric acid in excess precipitates the dissolved compound. Soluble in boiling nitric acid. Nearly insoluble in boiling hydrochloric acid. Water solutions of arsenious acid are not precipitated.

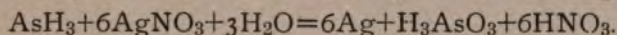
**94.** Silver nitrate in neutral solutions gives a yellow precipitate of silver arsenite,  $\text{Ag}_3\text{AsO}_3$ . Soluble in nitric acid and ammonium hydroxide. Slightly soluble in ammonium nitrate.

**95.** Copper sulphate in neutral solutions gives a yellowish-green precipitate of copper arsenite,  $\text{CuHAsO}_3$ . Soluble in alkali hydroxides and nitric acid.

**96.** Copper foil, heated with a solution containing hydrochloric acid, becomes coated with a film of iron-gray copper arsenide,  $\text{Cu}_5\text{As}_2$ . (Reinsch's test). By drying the coated

copper, after washing, and heating in a glass tube, a mirror of arsenic is obtained.

**97.** Zinc and sulphuric acid to which is added a solution containing arsenic, give hydrogen arsenide,  $\text{AsH}_3$ . The best method to pursue with this (Marsh's test) is to make an apparatus for generating hydrogen gas, with a drying tube attached filled with granulated calcium chloride, and a length of hard glass tubing terminating in a jet. The hard tube should be horizontal and the jet vertical. At various points on the horizontal tube the glass should be drawn out to make the tube smaller. When the apparatus is ready, place in it some zinc (free from arsenic) and cover it with water. Now pour in a little sulphuric acid (also free from arsenic) and shake the apparatus. Continue adding acid and shaking till a good supply of hydrogen gas is given off and all air is expelled from the apparatus. Now add the arsenic solution to be tested and heat the horizontal tube near the contracted parts, and on the side toward the hydrogen apparatus. The arsenic will form a black mirror on the tube just beyond the heated part. If the gas is ignited at the jet, and a piece of cold porcelain is held down in the flame, it will be coated with a mirror of arsenic. This mirror is soluble in <sup>a</sup> solution of calcium hypochlorite (bleaching powder); compare antimony **116**. On passing the gas through a solution of silver nitrate, a precipitate of silver is produced, and arsenious acid goes into solution according to the following equation:



By filtering off the precipitate, adding more silver nitrate to the filtrate, and carefully pouring on it a dilute solution of ammonium hydroxide, a yellow ring of silver arsenite will be formed at the junction of the two fluids. Compare antimony.

N. B.—Great care must be taken to insure the absence of arsenic in the zinc and sulphuric acid used in the Marsh test. It is best to test the gas by heating one part of the tube for some time before adding the arsenic solution. *It is also essential that the air in the apparatus be fully displaced by hydrogen before lighting the gas or heating the tube. Cover the apparatus with a towel before lighting the jet.*

**98.** Concentrated hydrochloric acid, an equal volume of a saturated solution of freshly prepared stannous chloride in concentrated hydrochloric acid, and a small piece of pure tin foil give a brown color or brown precipitate. Test facilitated by heating. (Bettendorff).

**99.** A solid piece of zinc, a small quantity of pure sulphuric acid, sp. gr. 1.835, about twenty times the volume of water, and then the solution to be tested, which should not be alkaline, are put in a test tube and the mouth immediately closed by placing over it a cap made of three thicknesses of filter paper, the upper one being moistened by a drop of a saturated water solution of silver nitrate acidulated with nitric acid. A bright yellow stain which becomes black or brown by application of water, shows the presence of arsenic. Antimony, under the same conditions, gives the black or brown at once, without first producing the yellow. (Gutzeit).

**100.** Fleitmann's test varies from the former by substituting potassium hydroxide test solution for the sulphuric acid. The solution containing the arsenic should not be acid. The cap is placed over the tube as before and the tube heated to about  $90^{\circ}$  C. A brown or black stain proves that arsenic is present. Antimony does not react.

**101.** Gatehouse's modification of Fleitmann's test consists in the substitution of aluminium for zinc.

#### ARSENIC COMPOUNDS.

**102.** Hydrogen sulphide and soluble sulphides, in acid solutions, give yellow precipitates of arsenic sulphide,  $As_2S_5$ , mixed with arsenious sulphide and sulphur. If mixed first with sulphurous acid and heated, and then with hydrogen sulphide, arsenious sulphide is precipitated.

**103.** Silver nitrate in neutral solutions gives a reddish-brown precipitate of silver arsenate,  $Ag_3AsO_4$ . Soluble in nitric acid and ammonium hydroxide. Slightly soluble in ammonium nitrate.

**104.** Copper sulphate in neutral solutions gives a greenish-blue precipitate of copper arsenate,  $\text{CuHAsO}_4$ . Soluble in nitric acid.

**105.** Magnesia mixture, in neutral or alkaline solutions, gives a white, crystalline precipitate of magnesium ammonium arsenate,  $\text{MgNH}_4\text{AsO}_4$ . Presence of arsenic in the precipitate may be proven by dissolving in a small amount of nitric acid, adding silver nitrate and carefully neutralizing with ammonium hydroxide, when a reddish-brown precipitate of silver arsenate will form.

**106.** Copper foil, same as with arsenious compounds.

**107.** Zinc and sulphuric acid, same as with arsenious compounds.

**108.** Molybdic acid in nitric acid, on heating, gives a bright yellow precipitate. Soluble in ammonium hydroxide from which solution magnesia mixture precipitates magnesium ammonium arsenate.

**109.** *Commercial Arsenic Compounds:*

Alloys:

Shot—Lead with 2% As.

Oxides and salts:

Arsenic—White arsenic— $\text{As}_2\text{O}_3$ , arsenious oxide.

Realgar— $\text{As}_2\text{S}_2$ , red orpiment.

Orpiment— $\text{As}_2\text{S}_3$ , yellow orpiment—King's yellow (mixture:  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{O}_3$ ).

Scheele's green—Copper arsenite,  $\text{CuHAsO}_3$ —Emerald green.

Paris green—Aceto-arsenite of copper, composition variable.

Sodium arsenate,  $\text{Na}_2\text{HAsO}_4$ —soluble 1 in 4 of water.

Fowler's solution—1% of arsenious oxide in potassium carbonate solution.

ANTIMONY.

*Blowpipe Test.*

**110.** Heated on charcoal with sodium carbonate, brittle metallic globules are obtained.

*Solution Tests.*

**111.** Hydrochloric acid and soluble chlorides react the same as with bismuth compounds.

**112.** Hydrogen sulphide and soluble sulphides in acid solutions, give orange-red precipitates of antimonious sulphide,  $\text{Sb}_2\text{S}_3$ . Soluble in alkali (K and Na) hydroxides, and sulphides, and strong hydrochloric acid. Slightly soluble in ammonium hydroxide. Nearly insoluble in ammonium carbonate. Insoluble in dilute hydrochloric acid.

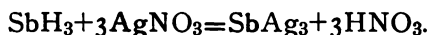
**113.** Alkali hydroxides give white precipitates of basic antimonious hydroxide,  $\text{SbOOH}$ . Soluble in excess of sodium and potassium hydroxides, and hot sodium and potassium carbonates, and acids excepting nitric. Nearly insoluble in excess of ammonia. Precipitation interfered with by tartrates.

**114.** Alkali carbonates give white precipitates of antimony hydroxide.

**115.** Zinc gives a black precipitate of antimony in the absence of nitric acid. If test is made in the presence of platinum foil, the zinc being in contact with the foil, a black stain is formed on the platinum. Soluble in nitric acid. Insoluble in hydrochloric acid.

**116.** Zinc and sulphuric acid, to which is added a solution containing antimony, give hydrogen antimonide,  $\text{SbH}_3$ . As in the case of arsenic, the best method to pursue in this test (Marsh's) is to make an apparatus for generating hydrogen gas, and to follow very carefully the directions given under arsenic for the same test, **97**. On heating the tube near the contracted parts, a black mirror will deposit in the same manner as with arsenic. By holding a piece of cold porcelain in the ignited jet of gas, a deposit similar to that obtained with arsenic will also be obtained; but in the case of the antimony mirror, the deposit is not soluble in solution of calcium hypochlorite (bleaching powder), compare arsenic, **97**. On passing the gas into a solution of silver nitrate, a black precipitate of silver antimonide,  $\text{Ag}_3\text{Sb}$ ,

will be obtained. This is formed according to the following equation :



By filtering off the precipitate and boiling it with a solution of hydrochloric and tartaric acids, filtering and passing hydrogen sulphide through the filtrate, an orange-red precipitate of antimonious sulphide is obtained. Very often a large part of the antimony is precipitated in the gas generator and if this deposit is treated in the same way as the preceding, the hydrogen sulphide will produce an orange-red precipitate.

**117.** Water precipitates basic salts, except in presence of a large amount of free acid.

**118. Commercial Antimony Compounds:**

Alloys:

Type metal—Antimony and lead.

Regulus—Commercial metallic antimony.

Britannia—Tin 80, antimony 10, with a little copper.

Oxides and salts:

Flowers of antimony— $\text{Sb}_2\text{O}_3$ .

Antimony ash— $\text{Sb}_2\text{O}_4$  from roasted sulphide.

Potassium metantimonate— $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$ , soluble in water.

Sodium metantimonate— $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$ , insoluble in water.

Butter of antimony— $\text{SbCl}_3$ .

Powder of algaroth— $\text{SbOCl}$ .

Antimony sulphide— $\text{Sb}_2\text{S}_3$ . Also called Antimony.

Kermes mineral— $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{S}_3$ .

Liver of antimony— $\text{K}_3\text{SbS}_3$ .

Tartar emetic— $2\text{KSbOC}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ .

**TIN.**

*Blowpipe Test.*

**119.** Heated on charcoal with sodium carbonate and potassium cyanide, globules of metal are obtained.

*Solution Tests.*

**120.** Hydrogen sulphide and soluble sulphides, in acid solutions, give brown precipitates of stannous sulphide,  $\text{SnS}$ , with stannous compounds; and yellow precipitates of stannic sulphide,  $\text{SnS}_2$ , with stannic compounds. Soluble in yellow ammonium sulphide and hot hydrochloric acid. Insoluble in ammonium carbonate.

**121.** Zinc in presence of hydrochloric acid gives a precipitate of heavy gray particles of metallic tin. Soluble in strong hydrochloric acid.

**122.** Mercuric chloride with stannous compounds gives a white precipitate of mercurous chloride, turning to black, due to the formation, by reduction, of metallic mercury.

**123.** Nitric acid and heat gives insoluble metastannic acid.

**124.** Sodium, potassium and ammonium hydroxides give white precipitates of stannous hydroxide,  $\text{Sn}(\text{OH})_2$ . Soluble in excess of sodium or potassium hydroxide. Insoluble in ammonium hydroxide and carbonates.

**125.** Alkali carbonates, same precipitate as the preceding.

**126. Commercial Tin Compounds:****Alloys:**

Britannia—Tin, 80; antimony 10, with a little copper.

Pewter—Tin and lead, 4 to 1.

Solder—Tin and lead, variable.

Bronze, gun metal, bell metal, speculum metal—Tin and copper in various proportions.

Block tin—Commercial metallic tin.

Tin or tin plate—Sheet iron covered with tin.

**Oxides and salts:**

Putty powder— $\text{SnO}_2$  with  $\text{PbO}$ .

Sodium stannate, dyers' mordant— $\text{Na}_2\text{SnO}_3$ .

Tin crystals, tin salts— $\text{SnCl}_2 + 2\text{H}_2\text{O}$ .

Nitromuriate of tin— $\text{SnCl}_4$ —Pink salt— $2\text{NH}_4\text{Cl} + \text{SnCl}_4$ .

Mosaic gold bronze powder— $\text{SnS}_2$ .

## CHAPTER V.

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### SEPARATION OF THE METALS OF THE SECOND GROUP.

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The group precipitate obtained by saturating with hydrogen sulphide the filtrate from the first group, should be well washed with water.

**127.** Break a hole in the lower part of the filter paper containing the precipitate and wash it off with about five times its volume of ammonium sulphide; shake well, filter, and wash the insoluble on the paper with water.

**128.** This treatment serves to separate this group into two parts, some of the members being dissolved by the ammonium sulphide, while others are not. Arsenic, antimony, and tin go into solution; lead, mercury, bismuth, copper, and cadmium are insoluble.

**129.** For treatment of solution containing arsenic, antimony, and tin, see *Sulphides Soluble in Ammonium Sulphide*, paragraph **145**.

#### SULPHIDES INSOLUBLE IN AMMONIUM SULPHIDE.

**130.** The insoluble on the filter is washed off with dilute nitric acid (1 part of concentrated acid and 2 parts of water) by breaking a hole in the lower part of the paper with a glass rod, and pouring the acid fluid through and through the paper until no more of the solid matter remains on it. This mixture of acid and insoluble is warmed and filtered. All the metals are dissolved with the exception of the mercury. The insoluble is washed with water, removed from the paper, treated with a few drops of aqua regia, and warmed to expel the excess of acid used. Dilute to three or four times its volume with water



and add stannous chloride, a white precipitate, sometimes changing to grayish-black proves the presence of *mercury*.

**131.** The fluid obtained by treating the sulphides insoluble in ammonium sulphide with dilute nitric acid and filtering, is evaporated to small bulk, best in an evaporating dish, and a few drops of it tested with dilute sulphuric acid, a white precipitate, settling rapidly, proves the presence of *lead*.

**132.** If lead is found by the above test, dilute sulphuric acid (about 15 drops of the concentrated acid and five times the quantity of water being a convenient amount to employ), is added to the balance of the fluid. This will precipitate out of the solution the lead, which is removed by filtering.

**133.** If lead is not found by testing as above, the treatment of the balance of the fluid with sulphuric acid is omitted.

**134.** The filtered fluid contains the other metals, bismuth, copper and cadmium, and is treated as follows:

**135.** Add ammonium hydroxide until the fluid is distinctly alkaline after shaking well. Filter out the precipitate formed and wash it three times with water.

**136.** Dissolve the washed precipitate on the paper with the smallest possible quantity of hydrochloric acid, allowing the acid fluid to run into a test tube. Boil down the acid fluid till only enough remains to allow one or two drops to be poured out. Pour this into a tube full of cold water. A fine white cloud proves the presence of *bismuth*.

**137.** If the filtrate obtained by adding ammonium hydroxide in excess and filtering, is blue, it proves the presence of *copper*. To this blue fluid, add potassium cyanide solution, a drop or two at a time, until the blue color *just disappears*, and then pass hydrogen sulphide through it. A yellow precipitate proves the presence of *cadmium*.

**138.** If the above filtrate is *not* blue, the treatment with potassium cyanide is omitted and cadmium is tested for directly with hydrogen sulphide.

The reasons for the steps taken in the separation of the metals of this section of the group are as follows :

**139.** After the treatment of the group precipitate with ammonium sulphide, there is left behind in an insoluble form the sulphides of lead, mercury, bismuth, copper, and cadmium. Dilute nitric acid has a solvent action on all of these with the exception of mercury. This sulphide is insoluble, while the others go into solution as nitrates.

**140.** The sulphide of mercury is dissolved in aqua regia and forms mercuric chloride which reacts with stannous chloride, producing mercurous chloride or metallic mercury which separates and serves as a test for this metal.

**141.** Having removed the mercury by this treatment, the filtrate containing the other metals is evaporated to small bulk to expel the excess of nitric acid, and a small part of it is treated with sulphuric acid. Lead if present will precipitate as lead sulphate. If lead is found, the balance of the fluid is mixed with sulphuric acid in excess, the lead is rendered insoluble by this treatment being in the form of lead sulphate, while the bismuth, copper, and cadmium are soluble.

**142.** The fluid is made alkaline with ammonium hydroxide, bismuth is precipitated as it is insoluble in excess of this reagent, whereas copper and cadmium are soluble, copper forming a blue fluid.

**143.** The precipitate containing the bismuth is washed to remove adhering salts in solution, dissolved in hydrochloric acid, and boiled to remove excess of acid, as the compound formed when it is poured into water, bismuth oxychloride, is soluble in excess of this acid.

**144.** The blue fluid containing the copper and cadmium is mixed with potassium cyanide solution until the blue color disappears, because in the presence of an excess of this reagent hydrogen sulphide will not give a precipitate with copper, while it will with cadmium.

## SULPHIDES SOLUBLE IN AMMONIUM SULPHIDE.

**145.** The fluid filtered from the insoluble matter after the treatment of the group precipitate with ammonium sulphide is now examined for arsenic, antimony, and tin.

**146.** These are thrown out of solution as sulphides by adding hydrochloric acid to the fluid, a few drops at a time, shaking after each addition, until it is acid.

**147.** Filter out the precipitate and wash it four or five times with water. The filtrate is rejected. If the precipitate is white, arsenic, antimony and tin are absent; the white precipitate being due to sulphur from the decomposition of the ammonium sulphide by the hydrochloric acid. If the color is other than white, one or more of this set may be present.

**148.** Break a hole in the lower part of the filter paper with a glass rod and wash the precipitate off the paper with about four times its volume of ammonium carbonate, pass and repass this same ammonium carbonate through the paper until all the precipitate is removed. Now warm gently, filter out the insoluble matter and wash it.

**149.** To the ammonium carbonate filtrate, add hydrochloric acid in excess. A bright yellow precipitate proves the presence of *arsenic*. Incomplete washing of the precipitate before the treatment with ammonium carbonate will sometimes account for the appearance here of a precipitate other than yellow. In this case, it is better to filter out the precipitate, wash it, and apply one or more of the special tests for arsenic before reporting it present. The best confirmatory test is that described in paragraph 91.

**150.** After washing the precipitate not dissolved by the ammonium carbonate, it is dried, scraped off the paper and transferred to an evaporating dish. It is then made thoroughly wet with hydrochloric acid. Heat the acid mixture until only yellow sulphur remains. Apply the heat carefully and do not let the material become dry. If the acid boils away, add more. Now dilute to about four times the volume with water. If the

addition of water causes the fluid to become milky, put in a few drops more of acid and warm until it is clear again. Filter and allow the fluid to run into another dish containing a clean piece of platinum foil and a clean piece of zinc. The best method of cleansing the platinum foil is to boil it first with nitric acid and afterwards heat it red hot in the flame. To clean the zinc allow it to be acted upon by some dilute hydrochloric acid. The zinc is placed on the platinum foil in the dish and the filtered fluid when added should cause a brisk evolution of gas. If it does not, add some hydrochloric acid. This action is allowed to continue for from ten to fifteen minutes. If a deep black deposit forms on the platinum, *antimony* is present. Tin also separates out and may adhere to the zinc. In order to prove the presence of tin, the platinum foil is removed from the solution and washed with water, the washings being added to the fluid in the dish. With the fingers, rub the adhering particles off the zinc into the fluid in the dish, using a little water from the wash bottle to wash the fingers.

**151.** Allow the solid matter in the dish to settle and carefully pour off the fluid, leaving the residue in the dish. To the residue add ten or fifteen drops of hydrochloric acid and heat gently. Pour the fluid into a test-tube after diluting with about four times the volume with water and filtering if necessary, and add a few drops of mercuric chloride. A white precipitate sometimes changing to grayish-black proves the presence of *tin*.

**152.** If antimony is not present, the deposit on the platinum foil may appear gray if tin is in the solution.

The reasons for the steps in the second part of this group are as follows :

**153.** The addition of hydrochloric acid to the ammonium sulphide filtrate neutralizes the solvent effect of the fluid, and the sulphides of arsenic, antimony, and tin are separated. The treatment with ammonium carbonate removes the arsenic which is soluble in this fluid, the antimony and tin not being affected. Hydrochloric acid destroys the solvent power of the ammonium

carbonate fluid, and yellow arsenic sulphide precipitates. Heating the sulphides insoluble in ammonium carbonate, with hydrochloric acid, changes them to chlorides. The milky appearance of the fluid sometimes obtained on adding water to the chloride solution, is due to the formation of antimony oxychloride, which is soluble in hydrochloric acid. The black stain on the platinum foil is metallic antimony, precipitated by the action of nascent hydrogen on the chloride ; the gray particles are metallic tin, due to the same action. Heating the gray particles of tin with hydrochloric acid gives stannous chloride and this reduces mercuric chloride, forming in the reduction mercurous chloride or metallic mercury, which precipitates.

TABLE II. H<sub>2</sub>S Group.

Add dilute (NH <sub>4</sub> ) <sub>2</sub> S, shake well, warm, filter and wash.	
<b>Insoluble.</b> —Warm with dilute HNO <sub>3</sub> (1 to 2). Filter and wash.	<b>Filtrate.</b> —Add HCl in slight excess, filter, wash ppt., and reject filtrate.
<b>Residue.</b> — Dissolve in a few drops of Aqua regia. Heat to expel excess of acid. Add Sn Cl <sub>2</sub> . A white to grayish-black ppt. <b>Hg.</b>	<b>Ppt.</b> —Warm with (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , filter and wash.
<b>Ppt.</b> —Pb SO <sub>4</sub> reject.	<b>Insoluble.</b> —Dry, scrape off paper, and boil with HCl till all dissolved except S, dilute with a little water, filter into dish, add Pt. and Zn. Black stains on Pt— <b>Sb.</b> Wash the black sediment, drain off the water, dry, add HCl and warm till dissolved. Dilute with a little water, put into test tube and add HgCl <sub>2</sub> . A white ppt. sometimes changing to grayish-black— <b>Sn.</b>
<b>Filtrate.</b> —Evaporate to small bulk and test a ppt. <b>Pb.</b> If lead is found, add dilute H <sub>2</sub> SO <sub>4</sub> to the balance of the fluid, stir well, and filter <sup>1</sup> .	<b>Filtrate.</b> —Add HCl in slight excess, filter, wash ppt., and reject filtrate.
<b>Ppt.</b> —Pb SO <sub>4</sub> reject.	<b>Insoluble.</b> —Dry, scrape off paper, and boil with HCl till all dissolved except S, dilute with a little water, filter into dish, add Pt. and Zn. Black stains on Pt— <b>Sb.</b> Wash the black sediment, drain off the water, dry, add HCl and warm till dissolved. Dilute with a little water, put into test tube and add HgCl <sub>2</sub> . A white ppt. sometimes changing to grayish-black— <b>Sn.</b>
<b>Filtrate.</b> —Make alkaline with NH <sub>4</sub> OH. Filter and wash well.	<b>Ppt.</b> —Dissolve in a few drops of HCl. blue — <b>Cu</b> <sup>2</sup> . Evaporate off excess of acid. Pour into cold water, White cloud— <b>B.</b>
<b>Ppt.</b> —Pb SO <sub>4</sub> reject.	<b>Filtrate.</b> — If blue — <b>Cu</b> <sup>2</sup> . Add KCN solution until blue color disappears, and then pass H <sub>2</sub> S gas. A yellow ppt. <b>Cd.</b>

1—If Pb is not found, treatment of balance of fluid with H<sub>2</sub>SO<sub>4</sub> can be omitted.

2—If not blue, Cu is absent and fluid is treated immediately with H<sub>2</sub>S. A yellow ppt.—**Cd.**



## CHAPTER VI.

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### SPECIAL TESTS FOR THE METALS OF THE THIRD GROUP.

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#### NICKEL.

##### *Blowpipe Test.*

**154.** Heated in a borax bead gives a seal brown color when cold.

##### *Solution Tests.*

**155.** Hydrogen sulphide in neutral and alkaline solutions gives a black precipitate of nickel sulphide,  $\text{NiS}$ . Soluble in aqua regia. Slightly soluble in ammonium sulphide. Insoluble in dilute hydrochloric acid and in acetic acid.

**156.** Ammonium sulphide gives the same precipitate as the preceding.

**157.** Sodium and potassium hydroxides give apple-green precipitates of nickel hydroxide,  $\text{Ni(OH)}_2$ . Soluble in ammonium carbonate giving a blue fluid; in hydrochloric, nitric, and sulphuric acids.

**158.** Ammonium hydroxide gives a precipitate of nickel hydroxide, dissolving in excess of the reagent producing a blue fluid.

**159.** Alkaline carbonates (of  $\text{K,Na}$ ) give green precipitates of nickel carbonate mixed with hydroxide. Insoluble in excess. Soluble in hydrochloric, nitric, and sulphuric acids.

**160.** Potassium ferrocyanide gives a greenish-white precipitate of nickel ferrocyanide,  $\text{Ni}_2\text{Fe(CN)}_6$ . Insoluble in hydrochloric acid.



**161.** Potassium ferricyanide gives a yellowish-brown precipitate of nickel ferricyanide,  $\text{Ni}_3\text{Fe}_2(\text{CN})_{12}$ . Insoluble in hydrochloric acid.

**162.** Potassium cyanide gives a yellowish-green precipitate of nickel cyanide,  $\text{Ni}(\text{CN})_2$ . Soluble in an excess of the precipitant. The cyanide solution thus obtained is reprecipitated by adding hydrochloric acid, giving nickel cyanide.

**163.** Bromine water or a solution of sodium hypochlorite added to a solution of nickel cyanide in potassium cyanide that is slightly acid with hydrochloric acid, and boiled, gives a black precipitate of nickelic hydroxide,  $\text{Ni}_2(\text{OH})_6$ .

**164.** Sodium phosphate gives a greenish-white precipitate of nickel phosphate. Soluble in acids.

**165.** Potassium nitrite in presence of acetic acid does not produce a precipitate.

**166.** *Commercial Nickel Compounds :*

*Alloys :*

German silver (Copper 100, Zinc 16, Nickel 40 parts).

Nickel coins (Copper, Zinc and Nickel; or Copper and Nickel).

*Salts :*

Double sulphate of nickel and ammonium  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 + 6\text{H}_2\text{O}$ .

Nickel sulphate.

Nickel chloride.

**COBALT.**

*Blowpipe Test.*

**167.** Heated in a borax bead gives an intense blue color.

*Solution Tests.*

**168.** Hydrogen sulphide in neutral or alkaline solutions gives a black precipitate of cobalt sulphide,  $\text{CoS}$ . Soluble in aqua regia. Insoluble in dilute hydrochloric acid and in acetic acid.

**169.** Ammonium sulphide gives the same precipitate as the preceding.

**170.** Sodium and potassium hydroxides precipitate basic cobalt hydroxide of various colors, dirty green when cold to pale red when hot; this latter compound is cobalt hydroxide,  $\text{Co}(\text{OH})_2$ . Insoluble in excess. Soluble in acids, ammonium hydroxide, and ammonium carbonate.

**171.** Ammonium hydroxide gives the same precipitate as the foregoing. Soluble in excess of the reagent forming a red fluid.

**172.** Sodium and potassium carbonates give pink precipitates of cobalt carbonate mixed with hydroxide. Insoluble in excess.

**173.** Potassium ferrocyanide gives a green precipitate of cobalt ferrocyanide,  $\text{Co}_2\text{Fe}(\text{CN})_6$ . Insoluble in hydrochloric acid.

**174.** Potassium ferricyanide gives a brownish-red precipitate of cobalt ferricyanide,  $\text{Co}_3\text{Fe}_2(\text{CN})_{12}$ . Insoluble in hydrochloric acid.

**175.** Potassium cyanide gives a brownish-white precipitate of cobalt cyanide,  $\text{Co}(\text{CN})_2$ . Soluble in excess of the precipitant. Hydrochloric acid precipitates the cyanide solution, giving cobalt cyanide.

**176.** Bromine water or a solution of sodium hypochlorite does not give a precipitate; differs from nickel compounds.

**177.** Potassium nitrite in the presence of acetic acid gives a yellow, crystalline precipitate of potassium cobaltic nitrite,  $\text{K}_6\text{Co}_2(\text{NO}_2)_{12} + 3\text{H}_2\text{O}$ . Soluble in water, but insoluble in the presence of the precipitant.

**178.** Sodium phosphate gives a purple precipitate of cobalt phosphate. Soluble in acids.

**179.** *Commercial Cobalt Compounds:*

Smalt is silicate of cobalt and potassium.

Zaffre is also a crude silicate of cobalt made by heating cobalt ore with sand.

Thenard's blue is phosphate of cobalt and aluminium.

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Cobalt ultramarine is another name for Thenard's blue.

Rinmann's green is a mixture of zinc and cobalt oxides.

Sympathetic ink is a solution of cobalt chloride.

Black oxide of cobalt is  $\text{Co}_2\text{O}_3$ .

Cobalt sulphate.

Cobalt chloride.

Cobalt nitrate.

## IRON.

### *Blowpipe Test.*

**180.** Heated in a borax bead ; in the oxidizing flame gives a yellow to red color while hot, colorless to yellow when cold ; in the reducing flame, a bottle-green color.

### *Solution Tests.*

#### FERROUS COMPOUNDS.

**181.** Hydrogen sulphide in neutral or alkaline solutions gives a black precipitate of ferrous sulphide,  $\text{FeS}$ . Soluble in nitric and acetic acids, and in dilute hydrochloric acid. Insoluble in alkali hydroxides and sulphides.

**182.** Ammonium sulphide gives the same precipitate as the preceding.

**183.** Alkali hydroxides give precipitates of ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , changing in color to green and reddish-brown when exposed to the air. Ammonium salts retard the precipitation by ammonium hydroxide. Organic acids, sugar, and like organic matters, retard or prevent the formation of the precipitate of hydroxide. Soluble in hydrochloric, nitric, and sulphuric acids.

**184.** Alkali carbonates give white precipitates of ferrous carbonate,  $\text{FeCO}_3$ , changing in color like the hydroxide. Soluble in hydrochloric, nitric, and sulphuric acids.

**185.** Potassium ferrocyanide gives a light blue precipitate of potassium ferrous ferrocyanide,  $\text{K}_2\text{Fe}.\text{Fe}(\text{CN})_6$ . Exposed to

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the air or treated with nitric acid, changes to ferric ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

**186.** Potassium ferricyanide gives a dark blue precipitate of ferrous ferricyanide,  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ . Decomposed by alkali hydroxides. Insoluble in hydrochloric acid.

**187.** Sodium phosphate gives a white precipitate of ferrous phosphate, changing to green. Soluble in acids.

**188.** Potassium sulphocyanate and barium carbonate produce no change.

#### FERRIC COMPOUNDS.

**189.** Hydrogen sulphide in acid solutions gives a milky precipitate of sulphur and reduction to ferrous compound. In alkaline or neutral solutions, a black precipitate of ferrous sulphide mixed with sulphur. Soluble in dilute hydrochloric acid. Insoluble in alkali hydroxides and sulphides.

**190.** Ammonium sulphide gives the same precipitate as the preceding.

**191.** Alkali hydroxides give reddish-brown precipitates of ferric hydroxide,  $\text{Fe}_2(\text{OH})_6$ . Prevented by organic matter. Soluble in hydrochloric, nitric, and sulphuric acids.

**192.** Alkali carbonates give the same precipitates as with the hydroxides.

**193.** Potassium ferrocyanide gives a dark blue precipitate of ferric ferrocyanide (Prussian Blue),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . Decomposed by alkali hydroxides. Insoluble in hydrochloric acid.

**194.** Potassium ferricyanide produces no precipitate but deepens the color.

**195.** Potassium sulphocyanate gives a blood red coloration.

**196.** Barium carbonate gives a reddish-brown precipitate of basic ferric hydroxide.

**197.** Sodium phosphate gives a white or yellowish-white precipitate of ferric phosphate,  $\text{Fe}_2(\text{PO}_4)_2$  in the presence of a

small amount of a soluble acetate. Insoluble in acetic acid. Soluble in hydrochloric, nitric, and sulphuric acids.

**198.** Sodium acetate in strong solution gives a dark red coloration, due to the formation of ferric acetate,  $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ .

**199. Commercial Iron Compounds :**

Pig iron is iron with carbon, silicon, phosphorus and sulphur as impurities.

Wrought or bar iron is nearly pure, but contains traces of the same impurities as pig iron.

Steel is the same as wrought iron with more or less carbon.

Spiegel-Eisen is an alloy of iron and manganese.

Ferrum reductum is metallic iron reduced by hydrogen from powdered ferric oxide.

Ochre is ferric oxide with more or less clay according to color.

Iron ore may be magnetite  $\text{Fe}_3\text{O}_4$ , hematite  $\text{Fe}_2\text{O}_3$ , or spathic iron (a basic carbonate).

Copperas is ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

Green vitriol is the same as preceding.

Both of these are often called "iron sulphate" or proto-sulphate.

Prussian blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

Liquor ferri chloridi contains ferric chloride.

Liquor ferri persulphatis contains ferric sulphate.

Iron scale preparations of U. S. P. contain ferric compounds.

Iron hypophosphite of U. S. P. is the ferric compound.

Iron pyrophosphate of U. S. P. is the ferric compound rendered soluble by sodium citrate.

Saccharated carbonate of iron of U. S. P. contains the ferrous compound.

Ammonia iron alum of U. S. P. contains the ferric compound.

Saccharated iodide of iron of U. S. P. contains the ferrous compound.

Lactate of iron of U. S. P. contains the ferrous compound.  
 Oxalate of iron of U. S. P. contains the ferrous compound.  
 Valerianate of iron of U. S. P. contains the ferric compound.

### MANGANESE.

#### *Blowpipe Tests.*

**200.** Heated in a borax bead in the outer flame gives amethyst color when hot, reddens on cooling; in inner flame is colorless.

**201.** Heated in a sodium carbonate bead in the outer flame gives a bluish-green color. Sodium nitrate assists the reaction.

#### *Solution Tests.*

**202.** Hydrogen sulphide in neutral or alkaline solutions gives a flesh colored precipitate of manganese sulphide,  $MnS$ , turning brown on exposure to the air. Soluble in hydrochloric, nitric, and acetic acids. Insoluble in ammonium sulphide and alkali hydroxides.

**203.** Ammonium sulphide gives the same precipitate as the preceding.

**204.** Sodium and potassium hydroxides give white precipitates of manganese hydroxide,  $Mn(OH)_2$ , turning brown when exposed to the air. Soluble in hydrochloric, nitric, and sulphuric acids, and ammonium chloride.

**205.** Ammonium hydroxide gives the same precipitate as the preceding. Prevented by ammonium chloride.

**206.** Alkali carbonates give white precipitates of manganese carbonate,  $MnCO_3$ , or a mixture of carbonate and hydroxide. Precipitation prevented by organic matter. Insoluble in excess.

**207.** Bromine water or sodium hypochlorite and a solution containing an excess of sodium or potassium hydroxide or acetate, heated, gives a black precipitate of manganese dioxide,  $MnO_2$ .

**208.** Potassium ferrocyanide gives a reddish-white precipitate of manganese ferrocyanide,  $Mn_2Fe(CN)_6$ . Soluble in hydrochloric acid.

**209.** Potassium ferricyanide gives a brown precipitate of manganese ferricyanide,  $\text{Mn}_3[\text{Fe}(\text{CN})_6]_2$ . Insoluble in hydrochloric acid and ammonium hydroxide.

**210.** Barium carbonate gives no precipitate except with sulphate, this forms manganese hydroxide and barium sulphate.

**211.** Sodium phosphate gives a white precipitate of manganese phosphate. Soluble in hydrochloric, nitric, sulphuric, and acetic acids.

**212.** *Commercial Manganese Compounds:*

Spiegel-Eisen is an alloy of manganese and iron.

Ferro-manganese is practically another variety of spiegel-eisen.

Black oxide of manganese is the dioxide of the metal; it is often called peroxide of manganese and sometimes "manganese."

Condy's green disinfectant is sodium manganate  $\text{Na}_2\text{MnO}_4$ .

Condy's red disinfectant is potassium permanganate  $\text{K}_2\text{Mn}_2\text{O}_8$ .

Manganous sulphate.

Manganous chloride.

## CHROMIUM.

### *Blowpipe Tests.*

**213.** Heated in a borax bead gives green color when cold.

**214.** Heated in a sodium carbonate bead, in the oxidizing flame gives yellow color; in reducing flame, yellowish-green color when cold.

### *Solution Tests.*

**215.** Ammonium sulphide in neutral or slightly acid solutions gives a green or bluish precipitate of chromium hydroxide,  $\text{Cr}_2(\text{OH})_6$ . Soluble in hydrochloric acid.

**216.** Ammonium hydroxide gives same precipitate as the preceding. Slightly soluble in excess of the reagent.

**217.** Sodium and potassium hydroxides precipitate chromium hydroxide. Soluble in excess of the reagents, reprecipitated by long boiling or by the addition of ammonium chloride.

**218.** Alkali carbonates precipitate basic chromium carbonate. Slightly soluble in large excess of the reagents. Soluble in hydrochloric acid.

**219.** Barium carbonate gives a green precipitate of basic chromium salt. Complete precipitation only takes place after long standing.

**220.** Organic matter interferes with the action of hydroxides and carbonates.

**221.** Bromine water or sodium hypochlorite and a solution containing an excess of sodium or potassium hydroxide, on boiling, the chromium is converted into chromic acid, which colors the fluid yellow.

**222.** Sodium phosphate gives a greenish precipitate of chromium phosphate. Soluble in acids.

**223.** *Commercial Chromium Compounds :*

Chrome yellow is lead chromate.

Chrome orange is basic lead chromate.

Bichromate of potassium is  $K_2Cr_2O_7$ ; it is also called Dichromate.

Chrome green is chromium oxide,  $Cr_2O_3$ .

## ZINC.

### *Blowpipe Test.*

**224.** Heated on charcoal, moistening in front of the compound with a solution of cobalt nitrate, and with the reducing flame gives a bright yellow-green coat when cold.

### *Solution Tests.*

**225.** Hydrogen sulphide has no action in acid solutions excepting those containing acetic acid when a white precipitate of zinc sulphide,  $ZnS$ , will be formed.

**226.** Ammonium sulphide gives a precipitate of zinc sulphide. Facilitated by the presence of ammonium chloride. Soluble in hydrochloric, nitric, and sulphuric acids. Insoluble in acetic acid, ammonium sulphide, and alkali hydroxides.



**227.** Sodium and potassium hydroxides give white precipitates of zinc hydroxide,  $\text{Zn(OH)}_2$ . Soluble in excess of the reagents. Reprecipitated by boiling unless the precipitants are in large excess. Soluble in hydrochloric, nitric, and sulphuric acids.

**228.** Ammonium hydroxide gives the same precipitate as the preceding. Readily soluble in excess of the reagent. Ammonium salts interfere with the precipitation.

**229.** Sodium and potassium carbonates give white precipitates of basic zinc carbonate,  $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 + 4\text{H}_2\text{O}$ . Insoluble in excess. Soluble in acids. Interfered with by ammonium salts.

**230.** Ammonium carbonate gives the same precipitate as the preceding. Soluble in excess.

**231.** Organic matter interferes with the precipitation of the hydroxide and basic carbonate.

**232.** Barium carbonate produces no precipitate except with the sulphate.

**233.** Potassium ferrocyanide gives a slimy white precipitate of zinc ferrocyanide,  $\text{Zn}_2\text{Fe(CN)}_6$ . Slightly soluble in an excess of the precipitant. Insoluble in hydrochloric acid.

**234.** Potassium ferricyanide gives a brownish-yellow precipitate of zinc ferricyanide,  $\text{Zn}_3[\text{Fe(CN)}_6]_2$ . Soluble in hydrochloric acid and ammonium hydroxide.

**235.** Sodium phosphate gives a white precipitate of zinc phosphate. Soluble in acids.

**236. Commercial Zinc Compounds :**

Spelter is metallic zinc.

Galvanized iron is sheet iron coated with zinc.

"Zinc" is the name often given to the calcined oxide of zinc.

Zinc white is the same as the preceding.

White vitrol is zinc sulphate,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ .

Colorless disinfecting fluids are usually zinc chloride mixed with other chlorides such as salt.

## ALUMINIUM.

*Blowpipe Test.*

**237.** Heated on charcoal and moistened with solution of cobalt nitrate gives a fine blue mass when cold.

*Solution Tests.*

**238.** Ammonium sulphide gives a white flocculent precipitate of aluminium hydroxide,  $\text{Al}_2(\text{OH})_6$ . Soluble in hydrochloric, nitric, and sulphuric acids.

**239.** Sodium and potassium hydroxides give precipitates of aluminium hydroxide. Soluble in excess of the reagents, and reprecipitated by ammonium chloride and heat.

**240.** Ammonium hydroxide gives the same precipitate as the preceding. Slightly soluble in excess of the reagent. Solubility lessened by the presence of ammonium salts.

**241.** Sodium and potassium carbonates give white precipitates of basic aluminium carbonate. Soluble in excess of the reagents and in acids.

**242.** Ammonium carbonate gives a precipitate of basic aluminium carbonate. Slightly soluble in excess of the reagent.

**243.** Barium carbonate gives a precipitate of basic salt with hydroxide. Not soluble in excess of the precipitant.

**244.** Sodium phosphate gives a white precipitate of aluminium phosphate,  $\text{AlPO}_4$ . Soluble in sodium and potassium hydroxides, hydrochloric, and nitric acids. Slightly soluble in ammonium hydroxide. Insoluble in acetic acid. Ammonium salts decrease its solubility in ammonium hydroxide. Ammonium chloride causes reprecipitation from its solution in sodium or potassium hydroxide.

**245. Commercial Aluminium Compounds :**

Aluminium bronze contains 10% of aluminium.

Roscone contains 30% aluminium with nickel, silver and tin.

Sunbronze contains 10% aluminium with cobalt and copper.

Metalline contains 25% aluminium with cobalt, iron and copper.

Romanium contains 95% aluminium with tungsten and nickel.

Alum is a double sulphate of aluminium and ammonium or potassium.

Kaolin is pure clay or aluminium silicate.

Lapis lazuli.

Ultramarine.

Sapphire.

Ruby.

Mica.

Aluminium acetate.

Aluminium sulphate.

## CHAPTER VII.

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### SEPARATION OF THE METALS OF THE THIRD GROUP.

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The group precipitate obtained by adding to the filtrate from the second group, ammonium chloride ( $\frac{1}{4}$  volume), ammonium hydroxide until alkaline, and ammonium sulphide in excess, should be washed with water.

**246.** Warm the precipitate with about four times its volume of diluted hydrochloric acid (one volume of the strong acid and two of water). Regulate the heat so that the mixture is slightly warm. Filter out the matter not dissolved and wash it. This contains the cobalt and nickel sulphides which are insoluble in dilute hydrochloric acid, while the iron, manganese, and zinc sulphides, together with the aluminium and chromium hydroxides go into solution as chlorides. Put the solution aside for the time being (See **250**). If it is pink, a little cobalt sulphide has dissolved.

**247.** If the material left undissolved is black, test in a borax bead (See **248**). If it is not black, cobalt and nickel are absent.

**248.** Make a loop on the end of a piece of platinum wire by winding it round the point of a lead pencil, heat the wire loop to redness, and while it is still hot, put it into some powdered borax. By this procedure the borax will adhere to the wire, and on heating it, a bead of clear borax glass will form in the loop. Care must be taken that the loop on the wire is not too large, an eighth of an inch in diameter is best. The bead must fill the loop and be as clear as glass and colorless. If it is colored or not clear, heat it till it melts and throw it off; a second trial will generally give a clear and colorless bead unless

the wire is very dirty. Having a good borax bead, dip it into the matter left undissolved by the hydrochloric acid, and heat it again till the bead is thoroughly melted and clear. Now look through the bead as a lens and note its color. If it is blue, *cobalt* is present, and perhaps nickel. If it is brown, *nickel* is present and no cobalt. Should the bead be opaque there is too much precipitate in it and more borax must be melted on it to make it show the color. In the last case heat the bead till it melts, throw off part of it, and, while it is still hot, dip it again into borax and remelt it.

**249.** If the bead is blue from the presence of cobalt, nickel *may* be present, its brown color being covered by the blue of the former metal. In this case the two metals must be separated by the following process: Dry the precipitate carefully and dissolve it, in a dish, in a few drops of aqua regia, boiling off the excess of acid and then dilute with a little water. Now add potassium cyanide solution (1 in 5), a few drops at a time, until the precipitate that first forms is just redissolved. If the solution after adding the cyanide becomes alkaline, add a drop or two of hydrochloric acid or enough to make it acid. Boil the mixture and if a precipitate forms add more cyanide, and if necessary, acid. At the end of the operation, the solution must be clear and slightly acid. The fluid is then boiled again and a solution of sodium hypochlorite added until it is alkaline and the boiling continued. Nickel will separate out as black hydroxide. This is filtered off, washed, and treated in a borax bead.

**250.** The solution obtained by treating the group precipitate with hydrochloric acid, which may contain the other metals of this group, is now examined. As stated above, these metals are present as chlorides. In the case of iron, it is in the form of ferrous chloride, and the first step is to convert it into ferric chloride, in order to precipitate it in the coming operations. For this purpose put the solution into a dish and add a small quantity of potassium chlorate. Boil the solution for some time, and, if it is cloudy, add a very little more chlorate. When finished, the fluid should be clear, and free from the odor of

chlorine. If by the boiling the fluid becomes concentrated, dilute with water. The volume should be the same at the end of the operation as it was in the beginning. Now add to the fluid in the dish, stirring constantly, sodium hydroxide until it is alkaline to red litmus paper. Then add *a little more* hydroxide and boil the mixture for some minutes. It is advisable to prepare the sodium hydroxide solution as needed by dissolving the solid in water. The precipitate contains iron, manganese and chromium as hydroxides, while zinc and aluminium go into solution, their hydroxides being soluble in the excess of the strong alkali used. Filter out the precipitate and wash it. Put the solution aside for the present (See 257).

**251.** Dry the precipitate just obtained; when dry, or nearly so, mix it with dry sodium carbonate. This is best done by scraping the dry precipitate from the paper with a clean pen-knife, and rubbing it in a small porcelain dish with the sodium carbonate by means of the small end of a pestle. The mixture should be dry and nearly white; if it is of a dark color more sodium carbonate must be added. If an insufficient quantity of carbonate is used the next steps give unsatisfactory results. *Time about 10 min.*  
*heat in a crucible. 254 next.*

**252.** Place the mixture just made on a piece of platinum foil held on a stick of charcoal, and by means of the blowpipe, heat it until it melts. Blow very cautiously in the beginning so as to avoid the scattering of the particles of the mixture. Having obtained a complete fusion of the mixture, place on one corner of it a small crystal of sodium nitrate, and heat the latter with the point of a blue blowpipe flame until it foams up, then remove the flame at once. Allow the fusion to cool. Note the color of the fusion at the point where the nitrate was fused and if it is bluish-green, it denotes the presence of *manganese*.

**253.** Having determined the presence or absence of manganese by the test with sodium nitrate just given, proceed to add more sodium nitrate to the fusion in small quantities, fusing on each addition until the entire mass has been made to foam up thoroughly. Allow the mass to cool, place it in a dish while

it is still attached to the platinum, add water and heat until the mass becomes detached from the foil. Remove the foil from the dish and wash with a small quantity of water, allowing the water to mix with the fluid in the dish. Boil the contents of the dish until the fusion has dissolved except perhaps some dark colored particles that readily settle. Filter out this dark material, wash it with water, reserve it (See 256) and examine the filtrate.

**254.** If the filtrate is yellow, make it acid with acetic acid and then add some lead acetate, a yellow precipitate is lead chromate and proves the presence of *chromium*.

**255.** Should the filtrate from the boiling of the fusion run through the filter colorless, chromium cannot be present, as all chromates are colored; therefore the addition of acetic acid and lead acetate may be omitted.

**256.** The dark colored material on the filter from the fusion solution (253), is dissolved off the paper by dropping on it a little hydrochloric acid, letting it run into a clean test-tube, in which it is heated until it is clear. Now dilute the acid solution with a little water and add to it a few drops of potassium sulphocyanate; a deep red color indicates the presence of *iron*. A pale orange color shows the presence of a trace of iron which will be found in a large number of substances as an impurity. The original substance should be examined by special tests to determine if ferrous or ferric compounds are present.

**257.** Now test the alkaline solution filtered from the precipitate 250 obtained after boiling with potassium chlorate and an excess of sodium hydroxide. This alkaline fluid is mixed with hydrochloric acid until, on shaking, it reddens blue litmus paper. It is then mixed with ammonium hydroxide until, after thoroughly shaking, it turns red litmus paper blue. Care must be taken not to add too large an excess of the reagent; to avoid this it should be added a few drops at a time until the fluid is *slightly* alkaline. The mixture is then heated to the

boiling point, a light flocculent precipitate shows the presence of *aluminium*.

**258.** If the precipitate is white, opaque and granular it may contain zinc, and must be allowed to settle, the fluid poured off, the precipitate dissolved in a few drops of hydrochloric acid, and ammonium hydroxide added in slight excess as before; if aluminium is present a light flocculent precipitate will now form. Filter off the precipitate and add the filtrate to the main solution.

**259.** If aluminium is proved to be present by paragraph 257, filter and add ammonium sulphide in small quantity to the filtrate and warm the mixture. If it is found necessary to perform the separation as described in paragraph 258, ammonium sulphide is added to the combined fluids. A white precipitate proves the presence of *zinc*.

**260.** If cobalt gave a pink color to the acid fluid after treating the group precipitate with dilute hydrochloric acid, the precipitate with ammonium sulphide for zinc may be dark colored. In this case, filter, reject filtrate, wash precipitate and treat it with dilute hydrochloric acid. To the acid filtrate thus obtained add ammonium hydroxide in excess, and then ammonium sulphide. A white precipitate is zinc sulphide.

The reasons for the steps taken for the separation of the metals of the third group are as follows :

**261.** The filtrate from the first group of metals is acid with hydrochloric acid used in excess to precipitate those metals. In order to obtain the metals of the third group this filtrate must be made alkaline, but before this is done, ammonium chloride is added to prevent the precipitation of magnesium hydroxide by the ammonium hydroxide which is used to make the filtrate alkaline. As the quantity of magnesium present is not known, add the ammonium chloride in good quantity to be sure to have enough. The addition of the ammonium chloride does not affect the reaction of the fluid. To make alkaline, add ammonium hydroxide until the fluid smells of it after being well



shaken. Next drop in ammonium sulphide, even if the ammonium hydroxide has already given a precipitate. This precipitate that is sometimes obtained on the addition of ammonium hydroxide may be partly the hydroxides of some of the metals of the third group and partly the sulphides of the same, due to the formation in the fluid of ammonium sulphide from the ammonium hydroxide uniting with the excess of the hydrogen sulphide used in precipitating the metals of the second group. If the filtrate from the third group precipitate is dark colored, it may contain nickel. In this case it should be submitted to a vigorous boiling and then filtered through the paper containing the group precipitate.

**262.** The first step in the treatment of the precipitate is for the purpose of separating the sulphides of cobalt and nickel from the rest of the sulphides and hydroxides of the group. That this separation may be perfect, the precipitate must be in the moist condition, as just precipitated. If it is dry, it may be that some of the sulphides or hydroxides will not dissolve in hydrochloric acid and thus remain with the sulphides of cobalt and nickel. Another important point is that the acid used should not be too strong, as in this case some of the nickel and cobalt sulphides may then pass into solution.

**263.** The test with the borax bead will show at once whether cobalt is present; but care must be taken that the bead first formed on the platinum wire is clear and colorless like glass. The presence of cobalt masks, by its color, the presence of nickel in the borax bead, therefore it is necessary to separate the nickel from the cobalt. The separation of the two metals depends on the formation of the double cyanides with potassium and the oxidation of the nickel to a black nickel hydroxide by means of bromine or sodium hypochlorite, which in the presence of a fixed alkali separates out as hydroxide, cobalt is not precipitated under these conditions.

**264.** The reasons for the course of procedure with the solution obtained from the treatment of the original sulphides with hydrochloric acid follow.

**265.** The fluid contains the excess of hydrochloric acid used on the group precipitate, also some hydrogen sulphide, together with the chlorides of the metals of the third group, the sulphides of which are soluble in hydrochloric acid. The iron chloride in this solution is in such a condition that it is not readily precipitated from solution, it is as the ferrous compound, and, in order to precipitate it, it must be changed to the ferric state. To accomplish this, add to the fluid a little potassium chlorate, and only so much as will just complete the change and no more. That sufficient is added is shown by the appearance of the fluid, it first becomes milky, and, as the action is completed, clears up. If iron is present, another change takes place; the fluid turns from colorless to yellow or brown, according to the amount of iron present. Boiling the fluid is for the purpose of driving off the chlorine compounds formed in the solution by the action of the potassium chlorate on the hydrochloric acid in it. These would interfere with the precipitation of the metals in the future. The next step is to add enough sodium hydroxide not only to precipitate the iron, chromium and manganese as hydroxides, but also to hold the aluminium and zinc in solution. The hydroxides of iron, chromium and manganese are insoluble in sodium hydroxide, while the hydroxides of aluminium and zinc are soluble. The chromium is at first dissolved by the alkali, but long boiling reprecipitates it. The zinc is held in solution by the use of a large excess of the reagent.

**266.** Having washed the precipitate and dried it, it is heated with a mixture of sodium carbonate and nitrate. This step is for the purpose of converting the chromium and manganese hydroxides into chromate and manganate of sodium. The former of these is yellow, the latter is bluish-green, and the depth of this latter color is so great that the mass may appear black if much manganese is present. This is the reason that only a small portion of the sodium nitrate is added at first to give a small depth of color. But a further addition of nitrate is necessary in order to completely convert the chromium into sodium chromate for its detection. Boiling the fused mass with water decomposes the

sodium manganate and leaves the sodium chromate unchanged; the sodium manganate decomposes into manganese dioxide, which remains insoluble with the iron, the latter being unchanged by the fusion and boiling. In case chromium is present the fluid will be yellow from the sodium chromate, but to make sure of the presence of chromium, acetic acid is added to the fluid until it is acid and then lead acetate, which should give a bright yellow precipitate of lead chromate. The matter insoluble after boiling the fused mass with water contains both manganese and iron, but as the former has already been tested for, it only remains to test for the latter, which is done by dissolving the insoluble matter in hydrochloric acid, boiling to expel chlorine formed by the action of the acid on the manganese dioxide present, and then adding potassium sulphocyanate. Here it should be remembered that the test for iron is an extremely delicate one, and a small change of color indicates only a trace of iron which is found in almost everything used in the laboratory. The iron as found by this test is no indication as to its form in the original solution, as it has been changed during the separation, therefore it is necessary to test the original fluid to determine whether it is present there in the ferrous or ferric condition.

**267.** The alkaline fluid which contains the aluminium and zinc is next examined. In order to neutralize the solvent action of the sodium hydroxide used, add hydrochloric acid in excess to this fluid and then an excess of ammonium hydroxide very carefully, to precipitate the aluminium as a hydroxide, zinc being soluble in an excess of this reagent. In doing this in cases where much zinc is present, a precipitate often forms of a different character from that obtained with aluminium; but a very slight acquaintance with the appearance of the two hydroxides will soon serve to distinguish them. If the precipitate obtained with ammonium hydroxide is opaque and granular it probably contains zinc; in this case make the fluid acid again with hydrochloric acid, then add ammonium hydroxide in excess, when the flocculent and light precipitate of aluminium hydroxide will

appear if that metal is present. The addition of ammonium sulphide to the filtrate from the aluminium hydroxide, or to the ammoniacal fluid if aluminium is absent, will give a white precipitate of zinc sulphide if that metal is present. In this case the color of the precipitate is very characteristic. It is also important to give the precipitate time to form if only small quantities of zinc are present ; slight warming of the fluid also aids the formation of zinc sulphide.

The preceding methods are tabulated in the following scheme :

TABLE III.  $(\text{NH}_4)_2\text{S}$  Group.

Treat with dilute HCl (1 in 3), filter and wash.

<b>Insoluble.</b> — Test in Borax bead.	<b>Filtrate.</b> —Boil in a dish with a <i>small crystal</i> of $\text{KClO}_3$ , continue boiling till Cl is gone. Add NaOH till strongly alkaline, boil again, filter and wash well.	
Blue bead indicates <b>Co.</b> Brown bead indicates <b>Ni.</b> If bead is blue <b>Ni</b> may also be present. Separate <b>Ni</b> & <b>Co</b> as per 249.	<b>Ppt.</b> —Dry, fuse with $\text{Na}_2\text{CO}_3$ and $\text{NaNO}_3$ . A green mass indicates <b>Mn</b> . Boil mass with water, filter and wash.	<b>Filtrate.</b> —Add HCl in slight excess, then $\text{NH}_4\text{OH}$ also in excess, warm, filter and wash.
<b>Insoluble.</b> — Dissolve in HCl, boil, dilute and add <b>KCNS</b> . Blood red color indicates <b>Fe</b> .	<b>Filtrate.</b> 1. Is <i>colorless</i> , indicates absence of <b>Cr</b> . Reject. 2. Is yellow. Add Acetic Acid in excess and then Lead Acetate. Yellow ppt. indicates <b>Cr</b> .	<b>Ppt.</b> —Light and flocculent is $\text{Al}_2(\text{OH})_6$ and indicates <b>Al</b> . If granular and white, dissolve in HCl, dilute solution, and add slight excess of $\text{NH}_4\text{OH}$ . Ppt. as above indicates <b>Al</b> .
		<b>Filtrate.</b> — Add $(\text{NH}_4)_2\text{S}$ , white ppt. is <b>Zn S</b> and indicates <b>Zn</b> .

## CHAPTER VIII.

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### SPECIAL TESTS FOR THE METALS OF THE FOURTH GROUP.

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#### BARIUM.

##### *Blowpipe Test.*

**268.** Heated on platinum wire gives a yellowish-green flame.

##### *Solution Tests.*

**269.** Hydrochloric or nitric acid, in small quantity, gives no result; if the acids are strong and are added in large quantity, white precipitates form which dissolve in water. This reaction is due to the fact that the chloride and nitrate of barium are insoluble in strong, but soluble in dilute acids.

**270.** Sodium and potassium hydroxides in very concentrated solutions produce white precipitates of barium hydroxide,  $\text{Ba}(\text{OH})_2$ . Soluble in water.

**271.** Sodium, potassium, and ammonium carbonates give white precipitates of barium carbonate,  $\text{BaCO}_3$ . In acid solutions the precipitation is incomplete, even with excess of the carbonates, until the solution is boiled. Slightly soluble in ammonium chloride. Soluble in hydrochloric, nitric and acetic acids.

**272.** Sulphuric acid and soluble sulphates give white precipitates of barium sulphate,  $\text{BaSO}_4$ . Slightly soluble in strong acids and in strong solution of ammonium salts not containing sulphuric acid or a sulphate. Insoluble in alkalies and dilute acids.

**273.** Calcium sulphate gives a precipitate of barium sulphate even in very dilute solutions.

**274.** Hydrofluosilicic acid gives a colorless, crystalline precipitate of barium silicofluoride,  $\text{BaSiF}_6$ . Test best made in a fluid containing alcohol. Slightly soluble in nitric and hydrochloric acids.

**275.** Sodium phosphate gives a white precipitate of barium phosphate,  $\text{BaHPO}_4$ . Soluble in acids. Slightly soluble in ammonium chloride.

**276.** Ammonium oxalate gives a white precipitate of barium oxalate,  $\text{BaC}_2\text{O}_4$ . Soluble in nitric and hydrochloric acids. Insoluble in acetic or oxalic acid unless just precipitated. Both the acetic and oxalic acid solutions quickly deposit acid barium oxalate,  $\text{BaH}_2(\text{C}_2\text{O}_4)_2$ , as a crystalline powder.

**277.** Potassium chromate and dichromate give yellow precipitates of barium chromate,  $\text{BaCrO}_4$ , even in dilute solutions. Soluble in nitric and hydrochloric acids. Insoluble in chromic and acetic acids.

**278.** *Commercial Barium Compounds:*

Barytes is barium sulphate found in nature.

Permanent white is barium sulphate.

Green fire is made with barium nitrate.

Natural barium carbonate (witherite) is said to be used for rat poison.

Barium chloride.

## STRONTIUM.

### *Blowpipe Test.*

**279.** Heated on platinum wire gives a lasting scarlet-red flame.

### *Solution Tests.*

**280.** Strong hydrochloric and nitric acids do not give precipitates.

**281.** Sodium and potassium hydroxides react in the same way as with barium.

**282.** Sodium, potassium, and ammonium carbonates give white precipitates of strontium carbonate,  $\text{SrCO}_3$ . If added to

an acid solution, the precipitation is only complete after boiling. Soluble in dilute acids. Slightly soluble in ammonium chloride.

**283.** Sulphuric acid and soluble sulphates give white precipitates of strontium sulphate,  $\text{SrSO}_4$ . Heat assists precipitation, addition of alcohol in the cold produces the same result. Slightly soluble in water, nitric and hydrochloric acids. Insoluble in solution of ammonium sulphate.

**284.** Calcium sulphate gives a white precipitate of strontium sulphate after standing for a short time.

**285.** Hydrofluosilicic acid produces no precipitate even in the presence of alcohol, unless the solution of the strontium salt is very concentrated.

**286.** Sodium phosphate gives a white precipitate of strontium phosphate,  $\text{SrHPO}_4$ . Soluble in dilute acids. Slightly soluble in ammonium chloride.

**287.** Ammonium oxalate gives a white precipitate of strontium oxalate,  $\text{SrC}_2\text{O}_4$ . Soluble in nitric and hydrochloric acids. Insoluble in acetic and oxalic acids unless just precipitated. Both the acetic and oxalic acid solutions quickly deposit acid strontium oxalate,  $\text{SrH}_2(\text{C}_2\text{O}_4)_2$ , as a crystalline powder.

**288.** Potassium chromate and dichromate give no precipitates unless the fluids tested are concentrated and neutral.

**289.** Ammonium sulphate gives a white precipitate of strontium sulphate.

**290.** *Commercial Strontium Compounds :*

The only compound of importance is the nitrate, which is used for red fire.

#### CALCIUM.

##### *Blowpipe Test.*

**291.** Heated on platinum wire gives a reddish-yellow flame.

##### *Solution Tests.*

**292.** Strong hydrochloric and nitric acids do not give precipitates.



**293.** Sodium and potassium hydroxides react in the same way as with barium.

**294.** Sodium, potassium, and ammonium carbonates give white precipitates of calcium carbonate,  $\text{CaCO}_3$ . If added to an acid solution, the precipitation is only complete after boiling. Soluble in dilute acids. Slightly soluble in ammonium chloride.

**295.** Sulphuric acid and soluble sulphates give no precipitates in dilute solutions. In strong solutions, sulphuric acid gives a white precipitate of calcium sulphate,  $\text{CaSO}_4$ ; precipitation assisted by alcohol. Soluble in acids, large amount of water, and boiling solution of ammonium sulphate.

**296.** Hydrofluosilicic acid gives no precipitate.

**297.** Sodium phosphate gives a white precipitate of calcium phosphate,  $\text{CaHPO}_4$ . Soluble in dilute acids. Slightly soluble in ammonium chloride.

**298.** Ammonium oxalate gives a white precipitate of calcium oxalate,  $\text{CaC}_2\text{O}_4$ . Soluble in hydrochloric and nitric acids. Insoluble in acetic and oxalic acids.

**299.** Potassium chromate and dichromate give no precipitates.

**300.** Ammonium sulphate gives no precipitate except in concentrated solutions.

**301. Commercial Calcium Compounds :**

Lime is calcium oxide; it is sometimes called quicklime.

Slaked lime is calcium hydroxide.

Air-slaked lime is a mixture of calcium hydroxide and carbonate.

Chalk is calcium carbonate.

Plaster of Paris is calcium sulphate.

Land plaster is calcium sulphate with water of crystallization.

Bone ash is calcium phosphate.

Bone black is a mixture of calcium phosphate and carbon.

Chloride of lime is calcium hypochlorite and chloride.

Bleaching powder is the same as the preceding.

## CHAPTER IX.

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### SEPARATION OF THE METALS OF THE FOURTH GROUP.

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The group precipitate obtained by adding to the filtrate from the third group, ammonium carbonate in excess, should be washed with water.

**302.** Dissolve the precipitate in a small quantity of warm, dilute acetic acid (1 in 3) by pouring the acid on the filter paper. After the fluid has run through, it is again poured on the paper. This second treatment being made to insure the complete dissolving of the precipitate.

**303.** To a *small* part of the acid fluid thus obtained, add a few drops of potassium chromate, a yellow precipitate proves the presence of *barium*. If a yellow precipitate is not formed barium is absent, and the balance of the fluid is treated according to paragraph **306**.

**304.** If barium is found by the above test, add potassium chromate in excess to the balance of the fluid. The reagent must be added until it ceases to give a precipitate. The solution is then filtered and the precipitate, which consists only of the barium in the form of a chromate, is rejected.

**305.** The filtrate, which contains the strontium and the calcium, is made alkaline by adding ammonium hydroxide and mixing until it turns red litmus paper to blue, it is then mixed with ammonium carbonate in excess and warmed. This serves to precipitate from the solution the strontium and calcium as carbonates. The precipitate is filtered off and washed with water, the filtrate and wash water being thrown away, as they

contain nothing but the reagents added in excess and ammonium salts formed in the operations.

**306.** The precipitate is dissolved in a small quantity of warm, dilute acetic acid, using the same method of dissolving as described in the beginning of the separation of the metals of this group. When solution is complete, the acid fluid is boiled, best in an evaporating dish, with a liberal amount of ammonium sulphate solution. Allow the boiling to continue for a few minutes but do not let the fluid become concentrated, dilute with water if necessary so that the volume at the end of the operation is about the same as that started with. The ammonium sulphate solution can be readily made by using forty drops of sulphuric acid, diluting with four or five times as much water, and adding ammonium hydroxide until alkaline.

**307.** After boiling, the mixture is filtered and the precipitate on the paper washed with water, and then tested for strontium by wetting a clean platinum wire with hydrochloric acid and then dipping it in the precipitate and finally heating in the flame; a lasting, deep crimson flame proves the presence of *strontium*. Before depending on this test as a conclusive one for this metal, the student should familiarize himself with the characteristics of the flame from strontium compounds as compared with what calcium gives under the same conditions.

**308.** The filtrate obtained after boiling with ammonium sulphate and filtering, is tested for calcium by adding to it a few drops of acetic acid and about ten or twelve drops of ammonium oxalate; a fine, white precipitate proves the presence of *calcium*. In a dilute solution the test may not be seen at first, the precipitate appearing after a short time as a fine, white cloud. Warming the fluid aids the formation of the precipitate.

The reasons for the steps taken in this separation are as follows:

**309.** The precipitate containing the metals of the group is dissolved in acetic acid as in this fluid the barium is completely precipitated by potassium chromate while the strontium and

calcium are not. If hydrochloric or nitric acid is used in place of the acetic, the barium could not be removed in this way.

**310.** As the precipitation of the barium by the chromate is complete, this metal in the form of a chromate is separated from the strontium and calcium by filtering. The fluid is made alkaline with ammonium hydroxide to get it in the proper condition for the precipitation of the remaining metals with ammonium carbonate; and it is warmed to insure the decomposition of acid carbonates of calcium and strontium, which are soluble, to the insoluble carbonates.

**311.** The precipitate cannot be tested conveniently for calcium and strontium, so it is dissolved in acetic acid. By boiling this acid fluid with ammonium sulphate, strontium sulphate is precipitated while the calcium remains in solution. If the boiling concentrates the mixture, dilution is necessary to prevent the precipitation of the calcium with the strontium, as in strong solution, ammonium sulphate precipitates calcium sulphate. This separation of calcium sulphate would not only tend to confuse the student when making the flame test for strontium, but later on when testing for calcium in its proper place, would be the cause of a very poor reaction and perhaps none at all.

**312.** Ammonium oxalate in an acetic acid solution precipitates the calcium as calcium oxalate as this salt is insoluble in the fluid.

**313.** If barium is not found, the addition of potassium chromate to the major part of the solution is not necessary, as this reagent is added to remove any barium so that its presence will not interfere in the separation and detection of the other members of the group. The major part of the fluid then contains only strontium and calcium in an acetic acid fluid and can be boiled immediately with ammonium sulphate to separate the strontium from the calcium.

TABLE IV.  $(\text{NH}_4)_2\text{CO}_3$  Group.

Dissolve in warm  $\text{HC}_3\text{H}_3\text{O}_3$  (1 in 3). Take small part of fluid and add a few drops of  $\text{K}_2\text{CrO}_4$ . A yellow precipitate proves Barium.\* If barium is found add  $\text{K}_2\text{CrO}_4$  in excess to balance of the fluid and filter.

**Precipitate.**— $\text{BaCrO}_4$  reject.

**Filtrate.**—Make alkaline with  $\text{NH}_4\text{OH}$ , and add  $(\text{NH}_4)_2\text{CO}_3$  in excess, warm, filter, and wash.

**Precipitate.**—Dissolve in warm  $\text{HC}_3\text{H}_3\text{O}_3$  (1 in 3) and boil in evaporating dish with a solution of  $(\text{NH}_4)_2\text{SO}_4$  for a few minutes. Filter and wash.

**Filtrate.**—Reject.

**Precipitate.**—Test on platinum wire **Filtrate.**—Add a few drops of  $\text{HC}_3\text{H}_3\text{O}_3$ , moistened with  $\text{HCl}$ .—Lasting crimson flame proves **Strontium**.

**Calcium.**

\* If barium is not found, the balance of the fluid is boiled in dish with ammonium sulphate, filtered, the precipitate tested for strontium, and the filtrate for calcium as above.

## CHAPTER X.

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### SPECIAL TESTS FOR THE METALS OF THE FIFTH GROUP.

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#### MAGNESIUM.

##### *Solution Tests.*

**314.** Ammonium hydroxide gives a white precipitate of magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ . Precipitation incomplete. Soluble in ammonium chloride and in acids.

**315.** Alkaline hydroxides (of K, Na, Ca and Ba) give precipitates of magnesium hydroxide. Precipitation promoted by boiling.

**316.** Ammonium carbonate gives a white precipitate of magnesium carbonate,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , or  $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . First is formed in the absence of ammonium salts, the second when the ammonium carbonate is in slight excess. Soluble in acids.

**317.** Sodium and potassium carbonates give white precipitates of basic magnesium carbonate,  $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$ . Soluble in ammonium chloride and in acids.

**318.** Sodium phosphate gives a white precipitate of magnesium hydrogen phosphate,  $\text{MgHPO}_4$ . This is formed only in the absence of ammonium salts. Soluble in acids.

**319.** Ammonium chloride, ammonium hydroxide, and finally sodium phosphate give a white, crystalline precipitate of magnesium ammonium phosphate,  $\text{Mg} \text{NH}_4 \text{PO}_4$ . In dilute solution, separates slowly, promoted by agitation. Soluble in hydrochloric, nitric, and acetic acids. Slightly soluble in water and in ammonium salts. Insoluble in dilute ammonium hydroxide.

**320.** Ammonium oxalate, in concentrated solutions gives magnesium oxalate,  $\text{Mg C}_2\text{O}_4$ ; in more dilute fluids, magnesium ammonium oxalate is formed. Presence of ammonium chloride and ammonium hydroxide interfere with the precipitation as oxalate.

**321.** Sulphuric acid gives no precipitate.

**322.** Hydrofluosilicic acid gives no precipitate.

**323.** Potassium chromate gives no precipitate.

**324.** *Commercial Magnesium Compounds :*

Epsom salt is magnesium sulphate.

Magnesia is magnesium oxide.

Magnesia alba is also magnesium oxide.

Magnesia ponderosa is magnesium oxide of a denser and more compact kind.

Light carbonate of magnesia is a mixture of magnesium carbonate and hydroxide. This is sometimes called magnesia levis.

Heavy carbonate of magnesia is also a mixture of carbonate and hydroxide. This is sometimes called magnesia ponderosa.

Dolomite is a variety of marble containing magnesium carbonate.

Asbestos is a magnesium silicate.

Talcum, meerschaum and serpentine are also silicates of this metal.

The "triple phosphate" found in urine is magnesium ammonium phosphate.

#### POTASSIUM.

##### *Blowpipe Test.*

**325.** Heated on platinum wire gives a violet or lilac flame.

##### *Solution Tests.*

**326.** Platinum chloride in acid or neutral solutions gives a fine, heavy, yellow precipitate of potassium platinum chloride,

$K_2PtCl_6$ . Precipitation assisted by stirring and by the addition of alcohol. Slightly soluble in water. Insoluble in alcohol.

**327.** Sodium acid tartrate, in concentrated solution gives a white, crystalline precipitate of potassium acid tartrate,  $KHC_4H_4O_6$ . Precipitation assisted by stirring. Soluble in acids and in alkali hydroxides.

**328.** Tartaric acid gives the same precipitate as in the previous test, if made under the same conditions.

**329.** Sodium cobaltic nitrite gives a heavy, yellow precipitate of potassium cobaltic nitrite.

**330.** *Commercial Potassium Compounds :*

Caustic potash is potassium hydroxide. Is sometimes called "potash."

Potashes are impure potassium carbonate and hydroxide from wood ashes.

Pearl ash is purified wood ashes and is a potassium carbonate.

Salt of tartar is potassium carbonate made from argols.

Saltpetre is potassium nitrate. Is sometimes called "nitre."

Cream of tartar is acid tartrate of potassium.

Soft soap is potassium soap.

Rochelle salt is double tartrate of potassium and sodium.

Hepar sulphurus or liver of sulphur is a mixture of potassium sulphides.

## SODIUM.

### *Blowpipe Test.*

**331.** Heated on a platinum wire gives an intense yellow flame.

### *Solution Tests.*

**332.** Platinum chloride gives no precipitate.

**333.** Sodium acid tartrate and tartaric acid give no precipitate.

**334.** Potassium pyroantimonate gives a white, granular



precipitate of sodium pyroantimonate,  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ . Test must be made in neutral or alkaline solutions.

**335. Commercial Sodium Compounds :**

Common or table salt is sodium chloride.

Soda used for washing is sodium carbonate with crystal water. Is sometimes called "soda crystals."

Sal soda is another name for washing soda or sodium carbonate crystals.

Caustic soda is sodium hydroxide.

Soda ash is crude sodium carbonate.

Glauber's salt is sodium sulphate with crystal water.

Chili saltpetre is sodium nitrate.

Sodium hyposulphite is sodium thiosulphate.

Phosphate of soda is disodium hydrogen phosphate.

Borax is sodium pyroborate.

Water glass is sodium silicate in strong solution.

Salt cake or nitre cake is sodium sulphate.

**AMMONIUM.**

*Solution Tests.*

**336.** Alkaline hydroxides (of K, Na, Ca, or Ba), warmed, cause the evolution of ammonia gas,  $\text{NH}_3$ , recognized by its odor or its action on test papers \*(litmus and mercurous nitrate).

**337.** Platinum chloride gives a fine, heavy, yellow precipitate of ammonium platonic chloride,  $(\text{NH}_4)_2\text{PtCl}_6$ . Appearance same as the corresponding potassium test. Insoluble in alcohol. Slightly soluble in water.

**338.** Sodium acid tartrate in concentrated solution gives a white, crystalline precipitate of ammonium acid tartrate,  $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ . Precipitation assisted by stirring. Soluble in acids and alkali hydroxides.

**339.** Tartaric acid gives the same precipitate as in the previous test. The test being made under the same conditions.

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\*Red litmus paper turns blue. Mercurous nitrate paper, black.

**340.** Nessler's reagent gives a reddish-brown precipitate of  $\text{Hg}_2\text{NH}_2\text{OI}$ . If only a small quantity of an ammonium compound is present, a yellowish-brown color is produced. This reaction is an extremely delicate one.

**341. *Commercial Ammonium Compounds :***

Gas liquor is a water solution of ammonium carbonate, sulphate and sulphide from the gas-works using soft coal.

A similar fluid is obtained in making boneblack.

Sal ammoniac is ammonium chloride.

Ammonia or spirits of hartshorn is a solution of ammonium hydroxide.

Carbonate of ammonia is a mixture of carbonate and carbamate. This is sometimes called "sal volatile."

Ammonia used in fertilizers is present as sulphate.



## CHAPTER XI.

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### SEPARATION OF THE METALS OF THE FIFTH GROUP.

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**342.** This group is contained in the filtrate obtained after precipitating the fourth group and filtering. This filtrate contains in addition to the metals of the group, all the reagents that have been used to precipitate the metals of the preceding groups with the exceptions of hydrochloric acid and hydrogen sulphide; therefore there are present ammonium chloride, hydroxide, sulphide and carbonate.

**343.** If the original material contained ammonium compounds this filtrate could not be used for their detection as these compounds have been added to it in the separations. It is therefore necessary to test for ammonium compounds by taking some of the original material, adding to it sodium hydroxide until it is *alkaline*, the top of the tube being closed with the thumb, and the contents warmed. By placing the tube under the nose and removing the finger, the odor of ammonia gas proves the presence of *ammonium* compounds.

**344.** The filtrate containing the metals of the fifth group is divided into two parts, one a small quantity and the other the balance of the fluid.

**345.** To the smaller portion sodium phosphate is added. If this gives a fine crystalline precipitate, it is magnesium ammonium phosphate, and indicates the presence of *magnesium*. If the precipitate is other than crystalline, magnesium is not present.

**346.** The larger portion of the fluid is evaporated to dryness in a porcelain dish. After the evaporation is complete, the dish

is heated over the flame and kept at a good heat until no more white fumes are seen ; during the operation of heating, the flame must be applied to all parts of the dish. This drives off all the ammonium compounds added in the previous operations.

**347.** Having expelled all volatile matter, allow the dish to cool, and then dissolve the residue in *a little water*. Filter the fluid through a very small paper into a clean test-tube. After filtration is complete, the amount of fluid in the tube should not exceed six drops, if it does, concentrate to this volume by boiling. Test some of the filtrate on a clean platinum wire in the Bunsen flame. A yellow flame indicates the presence of *sodium*. A lilac-colored flame indicates the presence of *potassium*.

**348.** If sodium is found by the flame test, there is no evidence that potassium is absent or present, because the yellow color of the sodium flame is so intense that it covers the potassium color. In this case, the flame may be observed through a blue glass, when the lilac color can be seen and the yellow is cut off. *In order to prove* the presence of potassium, put two or three drops of the fluid in a watch-glass, and add to it two or three times its volume of platinum chloride, stirring the mixture with a glass rod. A fine yellow precipitate of potassium platinum chloride (octohedra under a lens) indicates the presence of potassium in the fluid. The success of this latter test is dependent upon the complete driving off of the ammonium compounds by the heating of the dried mass in the porcelain dish. Ammonium compounds give the same colored precipitate with platinum chloride as the potassium compounds. ¶

**349.** If much magnesium is present, and the solution containing the sodium and potassium, after heating, is concentrated, it is best to add enough milk of lime to it to make it alkaline to red litmus paper ; then warm it and filter. This precipitates the magnesium as hydroxide. To the filtrate from the milk of lime, ammonium carbonate is added ; it is gently warmed, and then filtered. This filtrate is evaporated to dryness and heated to expel the ammonium salts, as explained above. The residue may now be dissolved in water and tested for sodium and potassium

as in **348**. This whole procedure may be omitted in a large majority of cases; for if only a moderate quantity of magnesium is present with the sodium and potassium, it will be made insoluble by heating (**346**), and little of it will pass into solution when the ignited residue is treated with water. A strong solution of magnesium chloride will give a precipitate with platinum chloride that resembles the potassium platinum salt.

The reasons for the method of procedure with the fluid containing the metals of the fifth group are as follows:

**350.** The alkaline filtrate is in the proper condition for the precipitation of magnesium with sodium phosphate. Only a small portion of the fluid is used for this test. The precipitate is a very characteristic one and will readily be recognized after once seeing it.

**351.** As the filtrate contains a large quantity of ammonium salts which have been added in the course of the separation of the metals of the first four groups, and as these ammonium salts interfere with one of the tests for potassium, they have to be removed before making the test. As all ammonium salts are volatile when heated, the evaporation of the balance of the filtrate not used for the magnesium test, and the heating of the dry residue, present a method of removing them without interfering with the sodium and potassium compounds present, which are not volatile when heated.

**352.** The testing of the water solution of the residue in the flame indicates if either sodium or potassium is present. But if sodium is present, potassium may also be with it and its color in the flame be masked by the bright yellow of the former metal. A piece of blue glass will often cut off the yellow flame of sodium and reveal the lilac color of potassium, but the test with platinum chloride should always be applied to make sure of the presence of potassium.

**353.** Platinum chloride gives, with ammonium salts, a fine yellow precipitate of ammonium platinum chloride, which it is practically impossible to distinguish from the potassium com-

pound by its appearance. It is therefore exceedingly important that all ammonium salts should be expelled by heat before making the test with platinum chloride as explained above. The white fumes obtained when heating the residue from the evaporation of the larger portion of the filtrate, are a guide as to the expulsion of ammonium salts; when the fumes cease, all these salts have volatilized.

**354.** The test for ammonium compounds made on the original material with sodium hydroxide depends on the fact that all ammonium salts are decomposed, and ammonia gas is evolved when they are heated with alkaline hydroxides. If the nose is not sensitive to small quantities of ammonia, moistened red litmus paper should be held over the mouth of the test tube so that the vapors pass it; it will be turned blue if ammonia gas is evolved.

## TABLE V. Alkali Group.

Divide Solution into two parts.

**Part I, Small.**—Add  $\text{Na}_2\text{HPO}_4$ . A fine crystalline ppt. is  $\text{MgNH}_4\text{PO}_4$  and indicates **Mg**.

**Part II, Large.**—Evaporate to dryness, heat till all white fumes cease. Cool, dissolve in water, filter out insoluble and reject it. Test solution on Pt wire in Bunsen flame. Yellow flame indicates **Na**. Observe flame through blue glass, lilac flame indicates **K**. Confirm presence of **K** by adding  $\text{PtCl}_4$  and alcohol to a few drops of solution in a W.G. Yellow ppt. on stirring indicates **K**.

**N. B.**— $\text{NH}_4$  salts must be looked for in the original solution before adding any reagents whatever. To test for  $\text{NH}_4$  salts add to the original solution an excess of  $\text{NaOH}$  and observe the odor of the gas evolved on warming. Pungent  $\text{NH}_3$  odor indicates  $\text{NH}_4$  salts.





—  
HC  
KL  
H<sub>2</sub>  
KC  
NF

Na  
K<sub>4</sub>  
H<sub>2</sub>  
K<sub>2</sub>  
—

—  
HC  
KI  
H<sub>2</sub>  
NI  
KC  
Cu  
K<sub>2</sub>  
Sn

—  
H<sub>2</sub>  
KI  
KI  
NI  
Cu  
Sn  
—

—  
H  
K  
H  
K



## CHAPTER XII.

### SPECIAL TESTS FOR ACID RADICALS OR ACIDS.

**355.** The words "acid radicals" are intended to convey to the mind the idea of that part of the formula of a salt remaining after the metal has been taken away. It must not be supposed that the combinations thus left have any existence; they only represent the salt formula from which the metal was removed. Thus, if the metal is taken away from the formula of any sulphate,  $\text{SO}_4$  is left, and this is the so-called radical of sulphuric acid. Again, if the metal is taken away from the formula of any nitrate,  $\text{NO}_3$  is left, and this is the radical of nitric acid. Or, in the case of any chloride, if the metal is taken away there is left only  $\text{Cl}$ , which is the radical of hydrochloric acid. In the case of any bromide,  $\text{Br}$  is left, and so on. Therefore the properties of the various acid radicals in the succeeding pages of this volume shall be studied, looking upon them as the representatives of the salts of the metals.

As in the case of the metals, only those acid radicals which are common, and which serve as illustrations of the methods of procedure shall be considered.

**356.** The following are the acid-radicals for which the special tests are given :

$\text{PO}_2$	of hypophosphites.	$\text{Br}$	of bromides.
$\text{ClO}_3$	" chlorates.	$\text{I}$	" iodides.
$\text{NO}_2$	" nitrites.	$\text{Fe}_2(\text{CN})_{12}$	" ferricyanides.
$\text{NO}_3$	" nitrates.	$\text{Fe}(\text{CN})_6$	" ferrocyanides.
$\text{S}$	" sulphides.	$\text{Cl}$	" chlorides.
$\text{SO}_3$	" sulphites.	$\text{CrO}_4$	" chromates.
$\text{CN}$	" cyanides.	$\text{AsO}_3$	" arsenites.

$\text{CO}_3$	of carbonates.	$\text{AsO}_4$	of arsenates.
$\text{S}_2\text{O}_3$	" thiosulphates.	$\text{PO}_4$	" phosphates.
$\text{BO}_3$	" borates.	$\text{SO}_4$	" sulphates.
$\text{C}_2\text{H}_3\text{O}_2$	" acetates.	$\text{C}_2\text{O}_4$	" oxalates.
F	" fluorides.	$\text{C}_4\text{H}_4\text{O}_6$	" tartrates.
$\text{SiO}_3$	" silicates.	$\text{C}_6\text{H}_5\text{O}_7$	" citrates.

#### HYPOPHOSPHITES.

##### *Test on Dry Substance.*

**357.** Heated in dry vessels decompose giving off a gas, which takes fire when brought in contact with the air and which has a characteristic garlic-like odor.

##### *Solution Tests.*

**358.** Silver nitrate gives a white precipitate of silver hypophosphite, rapidly becoming black, due to the formation of metallic silver.

**359.** Mercuric chloride and hydrochloric acid produce a precipitate of white mercurous chloride, which on heating, turns gray-black, due to the formation of metallic mercury.

**360.** Ammonium molybdate gives a fine blue precipitate.

#### CHLORATES.

##### *Tests on Dry Substance.*

**361.** Heated on charcoal produce deflagration. It is necessary to heat the charcoal in contact with the substance.

**362.** Heated, when not in contact with organic material, oxygen is liberated and a chloride is formed, which when dissolved gives the tests for this radical (see chlorides).

**363.** Dropped on sulphuric acid in a watch glass, the acid is colored yellow and at the same time chlorine oxides are evolved which may be recognized by their odor. The test should be made on a small scale, as a compound is formed which is explosive.

**364.** Hydrochloric acid evolves chlorine and small quantities of chlorous oxide.

*Solution Tests.*

**365.** Reduced to chlorides by zinc-copper couple. Allow the action to continue for some minutes, add nitric acid and silver nitrate, a white precipitate is obtained. If chlorides, bromides, &c. are present these must first be removed by adding silver nitrate in excess before applying the above test.

**366.** Hydrochloric acid will react in the same way with concentrated solutions as with the dry salt. See **364**.

**367.** Solution of potassium iodide containing starch, and acid with acetic acid produces no change; but on addition of hydrochloric acid, a blue color is obtained.

NITRITES.

*Tests on Dry Substance.*

**368.** Decomposed by hydrochloric or sulphuric acid, with effervescence and the liberation of a gas, recognized by its color when mixed with air, and its odor.

**369.** Heated on charcoal, deflagration takes place the same as with nitrates.

**370.** Sulphuric acid and ferrous sulphate give the same result as with nitrates, see **379**. Ferrous sulphate alone will give the colored ring.

*Solution Tests.*

**371.** Silver nitrate in strong solutions gives a white precipitate of silver nitrite,  $\text{AgNO}_2$ .

**372.** Mixing the fluid with a small quantity of sulphuric acid and adding a few drops of this mixture to a solution containing potassium iodide and starch, a blue coloration results due to the decomposition of the potassium iodide, liberating iodine which reacts with the starch.

**373.** The addition of acetic acid in excess, followed by a solution of potassium sulphocyanate, and finally by nitric acid;

a deep red coloration results. Heating causes the color to disappear. The color is due to the formation of nitryl,  $\text{NO}_2$ . In making this test it is necessary to prove the absence of all substances which would have a reducing action upon nitric acid.

**374.** The addition of indigo solution to water until the transparency disappears, then hydrochloric acid and afterwards a solution of an alkali polysulphide until the blue color just vanishes and filtering; the addition of a nitrite to this mixture causes the re-appearance of the blue coloration.

**375.** Pyrogallol in solutions acidified with sulphuric acid, gives a brown color. Nitrates give no reaction.

#### NITRATES.

##### *Tests on Dry Substance.*

**376.** Heated on charcoal produce deflagration. It is necessary to heat the charcoal in contact with the substance.

**377.** Sulphuric acid produces decomposition with the formation of nitric acid.

**378.** Copper and sulphuric acid give fumes which become reddish-brown in contact with air, due to the formation of nitrogen tetroxide.

**379.** Sulphuric acid followed by the careful addition of a solution of ferrous sulphate forms at the junction of the two fluids, a purplish to dark brown ring. Iodides, bromides, chlorates and chromates interfere with the test.

##### *Solution Tests.*

**380.** Nitric acid placed in contact with nitrogenous organic bodies, as feathers, wool, skin, etc., produces an intense yellow color. Heat promotes the action.

**381.** Reduced to nitrites by zinc amalgam; and the after addition of sulphuric acid, potassium iodide, and starch paste produces a blue color. The nitrous acid, set free by the sulphuric acid, liberates iodine, which gives the blue with starch.

**382.** Reduced to ammonium compounds by a zinc-copper couple (formed by adding a few drops of copper sulphate to a solution containing a piece of sheet zinc), and the after addition of sulphuric acid. Allow the action to go on for some minutes and test in the ordinary way for ammonium compounds with sodium hydroxide.

**383.** One drop of hydrochloric acid, one drop of a ten per cent. resorcin solution, and about 2 cubic centimeters of pure sulphuric acid; a purple color results.

**384.** Sulphuric acid and ferrous sulphate give the same result as with the dry salt, provided the solution is concentrated.

**385.** Decomposed so as to form nitric acid and then dropped on a crystal of brucine, a deep red color is obtained.

**386.** A few drops of the fluid to be tested are evaporated on a water bath and while still hot a mixture prepared by dissolving one part of phenol in four parts of sulphuric acid and diluting with two parts of water is added; a reddish color is produced.

#### SULPHIDES.

##### *Test on Dry Substance.*

**387.** Soluble salts with dilute hydrochloric or sulphuric acid give an effervescence due to the liberation of hydrogen sulphide. Recognized by its odor and by its action on paper moistened with a solution of a lead or silver salt, which the gas turns dark in color.

##### *Solution Tests.*

**388.** Silver nitrate gives a black precipitate of silver sulphide,  $\text{Ag}_2\text{S}$ . Soluble in potassium cyanide and in boiling nitric acid. Insoluble in dilute acids, alkali hydroxides and sulphides.

**389.** Lead acetate gives a black precipitate of lead sulphide,  $\text{PbS}$ . Insoluble in cold dilute acids, alkali hydroxides and sulphides, and in potassium cyanide.

**390.** Sodium nitroprusside added to a solution containing the sulphide and sodium hydroxide gives a violet-red color.



This reaction is very delicate and can be applied by moistening filter paper with the necessary reagents and using this paper for the test.

#### SULPHITES.

##### *Test on Dry Substance.*

**391.** Dilute hydrochloric or sulphuric acid gives an effervescence due to the liberation of a gas, sulphur dioxide. Detected by its odor, that of burning sulphur; and its action on organic coloring matter, which it bleaches.

##### *Solution Tests.*

**392.** Barium chloride gives a white precipitate of barium sulphite,  $\text{BaSO}_3$ . Soluble in hydrochloric acid.

**393.** Silver nitrate gives a white precipitate of silver sulphite,  $\text{Ag}_2\text{SO}_3$ . Soluble in nitric acid.

**394.** Hydrogen sulphide decomposes acid solutions, sulphur separating.

**395.** Zinc and sulphuric acid in a hydrogen generator, with a sulphite, evolve hydrogen sulphide which may be detected in the ordinary way. Before making the test it should be ascertained that the zinc and sulphuric acid alone do not give the reaction.

#### CYANIDES.

##### *Test on Dry Substance.*

**396.** Soluble salts with dilute hydrochloric or sulphuric acid give an effervescence due to the liberation of hydrocyanic (prussic) acid, which has a characteristic odor, somewhat like bitter almonds.

##### *Solution Tests.*

**397.** Silver nitrate gives a white precipitate of silver cyanide,  $\text{AgCN}$ . Soluble in ammonium hydroxide and potassium cyanide. Insoluble in dilute nitric acid. Decomposed by gentle ignition producing metallic silver.

**398.** Ferrous sulphate and a few drops of ferric chloride added to a solution of a cyanide made acid with hydrochloric acid, and followed by sodium hydroxide in excess and heated for a few minutes give a bluish-green precipitate. If this mixture is now made acid with hydrochloric acid, a blue precipitate of ferric ferrocyanide remains undissolved. In dilute solutions the fluid is green after adding the acid, but on standing a blue precipitate settles down.

**399.** Ammonium sulphide (yellow) added until the fluid is yellow, followed by ammonium hydroxide, gives ammonium sulphocyanate when the mixture is warmed to expel excess of ammonium sulphide. By making this fluid acid with hydrochloric acid and adding ferric chloride, a blood-red color is obtained.

**400.** The careful addition of a solution of copper sulphate to an alkali cyanide produces a beautiful rose-pink coloration.

#### CARBONATES.

##### *Test on Dry Substance.*

**401.** Decomposed by all acids excepting hydrocyanic and hydrosulphuric with the evolution of carbon dioxide. This gas passed through lime water gives a precipitate of calcium carbonate.

##### *Solution Tests.*

**402.** Barium hydroxide gives a white precipitate of barium carbonate,  $\text{BaCO}_3$ . Soluble in acids with effervescence.

**403.** Barium chloride gives a white precipitate of barium carbonate. Solutions containing carbon dioxide not combined with a metal are not precipitated.

**404.** Calcium hydroxide gives a white precipitate of calcium carbonate,  $\text{CaCO}_3$ . Soluble in acids with effervescence.

**405.** Calcium chloride gives the same precipitate as the preceding. Solutions containing carbon dioxide not combined with a metal are not precipitated.

## THIOSULPHATES.

*Tests on Dry Substance.*

**406.** Decomposed by dilute hydrochloric and sulphuric acids, sulphur dioxide being evolved and sulphur separating as a white or yellowish precipitate.

**407.** Same reaction on silver coin after fusing on charcoal with sodium carbonate as a sulphate.

*Solution Tests.*

**408.** Barium chloride gives a white precipitate of barium thiosulphate,  $\text{BaS}_2\text{O}_3$ . Soluble in hydrochloric acid with evolution of sulphur dioxide and separation of sulphur.

**409.** Silver nitrate gives a white precipitate rapidly becoming dark in color. The first precipitate is silver thiosulphate,  $\text{Ag}_2\text{S}_2\text{O}_3$ ; the dark one, silver sulphide,  $\text{Ag}_2\text{S}$ .

**410.** Ferric chloride produces a reddish-violet coloration which disappears slowly.

**411.** Hydrogen sulphide passed through a slightly acid solution gives a separation of sulphur.

## BORATES.

*Tests on Dry Substance.*

**412.** Mixed with sulphuric acid so as to form a paste and placed in a loop of platinum wire which has been moistened with glycerine, and heated with the blowpipe flame, gives a fine grass-green flame which is of short duration.

**413.** Made into a paste with water, mixed with potassium acid sulphate and calcium fluoride ( $4\frac{1}{2}$  of the former and 1 of the latter) and heated with the blowpipe; a green flame is obtained.

*Solution Tests.*

**414.** Made acid with sulphuric acid and then mixed with alcohol and ignited, a green flame results.

**415.** Barium chloride in strong solutions gives a white precipitate of barium borate. Soluble in large excess of water, in acids, and in ammonium salts.

**416.** Silver nitrate in strong solutions gives a precipitate of silver borate. This is yellowish, due to some silver oxide mixed with it. Soluble in acids and ammonium salts.

**417.** Turmeric paper moistened with a solution of a borate that is just acid with hydrochloric acid, and dried at  $100^{\circ}\text{C}$ , shows a peculiar red color that is very characteristic. Care must be taken not to have much hydrochloric acid present as this will change the original color of the paper.

**418.** Calcium chloride rendered slightly alkaline with ammonium hydroxide and heated, gives a white precipitate of calcium borate. Soluble in acetic acid.

#### ACETATES.

##### *Test on Dry Substance.*

**419.** Decomposed by heat, some giving a carbonized residue others giving acetone and leaving behind a carbonate, while the ammonium compound is completely volatilized.

##### *Solution Tests.*

**420.** Ferric chloride in solutions which are neutral or contain very little acetic acid gives a reddish-brown precipitate on boiling. Before boiling, the fluid has a deep red color. Color discharged by hydrochloric acid and mercuric chloride.

**421.** Silver nitrate in neutral solutions gives a white crystalline precipitate of silver acetate,  $\text{AgC}_2\text{H}_3\text{O}_2$ . Soluble in ammonium hydroxide, slightly so in cold water, more soluble in hot water from which it crystallizes on cooling.

**422.** Mercurous nitrate gives a white, scaly precipitate of mercurous acetate,  $\text{Hg}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ . Soluble in hot water from which it crystallizes on cooling, slightly soluble in an excess of the precipitant, in cold water, and in acetic acid.

**423.** Alcohol and sulphuric acid produce acetic ether, recognized by its odor. The mixture is warmed gently after the addition of the two reagents.

#### FLUORIDES.

##### *Tests on Dry Substance.*

**424.** Sulphuric acid causes the evolution of hydrofluoric acid which etches glass. Test is best made in a lead or platinum vessel covered with glass coated with wax which has been removed in a few places, exposing some of the glass to the action of the acid fumes. After allowing the action to go on for some time and then removing the wax, the etched portion can be easily seen.

**425.** Heated with sulphuric acid and silica and the fumes condensed by a drop of water upon a platinum wire, a film of silicic acid will form upon the water.

##### *Solution Tests.*

**426.** Barium chloride gives a white, bulky precipitate of barium fluoride,  $\text{BaF}_2$ . Soluble in hydrochloric and nitric acids, and in ammonium salts. Insoluble in water.

**427.** Calcium chloride gives a whitish, nearly transparent precipitate of calcium fluoride,  $\text{CaF}_2$ . Precipitation promoted by ammonium hydroxide. Insoluble in water and in alkaline liquids.

#### SILICATES.

##### *Tests on Dry Substance.*

**428.** Heated in a bead of sodium metaphosphate, an insoluble skeleton of silica is obtained.

**429.** Fused with a mixture of sodium and potassium carbonates, sodium and potassium silicates are formed which are soluble in water.

##### *Solution Tests.*

**430.** Acids decompose the silicate, producing silicic acid. In dilute fluids this compound may remain in solution or may

separate as a gelatinous precipitate. If the acid mixture is evaporated to dryness and then heated at a temperature of about  $110^{\circ}$  C., and treated with acid again, the metals will go into solution and insoluble silica,  $\text{SiO}_2$ , will remain.

**431.** Ammonium chloride precipitates silicic acid in solutions containing alkali silicates, if they are not too dilute.

#### BROMIDES.

##### *Tests on Dry Substance.*

**432.** Strong nitric acid and heating give reddish-brown vapors of bromine. Some insoluble bromides are not decomposed.

**433.** Sulphuric acid and heating give the same reaction as the former.

**434.** Manganese dioxide and sulphuric acid, and heat, evolve bromine. These vapors, passed into cold starch solution or allowed to act upon starch paper, give a yellow color.

##### *Solution Tests.*

**435.** Silver nitrate gives a yellowish-white precipitate of silver bromide,  $\text{AgBr}$ , becoming dark in color on exposure to sunlight. Soluble in potassium cyanide, slightly soluble in ammonium hydroxide. Insoluble in nitric acid.

**436.** Chlorine (either as a gas or in solution) liberates bromine which colors the fluid yellow. Care must be taken in applying this test, as too much chlorine will cause the color to disappear, owing to the formation of bromine chloride.

**437.** Carbon disulphide, chloroform, or ether added to a solution containing free bromine, dissolves it out of the fluid on mixing thoroughly, and becomes yellowish-brown to red.

#### IODIDES.

##### *Tests on Dry Substance.*

**438.** Nitric acid and heat give violet vapors of iodine. Some insoluble iodides are not decomposed.

**439.** Sulphuric acid and heat give the same result as in the former test.

**440.** Manganese dioxide, sulphuric acid, and heat evolve iodine. These vapors passed into cold starch solution or allowed to act upon starch paper, give a deep blue color.

*Solution Tests.*

**441.** Silver nitrate gives a yellowish-white precipitate of silver iodide,  $\text{AgI}$ , becoming dark in color on exposure to sunlight. Soluble in potassium cyanide and in a concentrated solution of potassium iodide. Very slightly soluble in ammonium hydroxide. Insoluble in alcohol and dilute acids.

**442.** Copper sulphate 1 part with ferrous sulphate  $2\frac{1}{2}$  parts, in a neutral solution, gives a dirty white precipitate of cuprous iodide,  $\text{Cu}_2\text{I}_2$ . Precipitation assisted by the addition of a small quantity of ammonium hydroxide. Chlorides and bromides do not affect this reaction.

**443.** Chlorine (either as a gas or in solution) liberates iodine which may color the fluid reddish-brown, or may separate as a dark colored precipitate, depending on the quantity set free. Care must be taken in applying this test, as too much chlorine will cause the color to disappear, owing to the formation of iodine chloride.

**444.** Cold starch paste gives an intense blue color with liberated iodine.

**445.** Carbon disulphide, chloroform, or ether dissolves iodine and becomes violet in color.

**446.** Palladious chloride or nitrate gives a black precipitate of palladious iodide,  $\text{PdI}_2$ . Decomposed somewhat below  $350^\circ\text{C}$ . into iodine and palladium.

**447.** Mercuric chloride gives a red precipitate of mercuric iodide,  $\text{HgI}_2$ . For properties of precipitate, see paragraph 59.

**448.** Lead nitrate gives a yellow precipitate of lead iodide,  $\text{PbI}_2$ . For properties of precipitate, see paragraph 23.

## FERRICYANIDES.

*Test on Dry Substance.*

**449.** Decomposed when heated to redness.

*Solution Tests.*

**450.** Ferric chloride does not precipitate these solutions.

**451.** Ferrous sulphate gives a blue precipitate of ferrous ferricyanide,  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ . Insoluble in hydrochloric acid. Decomposed by alkaline hydroxides.

**452.** Copper sulphate gives a yellowish-green precipitate of copper ferricyanide,  $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$ . Insoluble in hydrochloric acid.

**453.** Silver nitrate gives an orange precipitate of silver ferricyanide,  $\text{Ag}_6[\text{Fe}(\text{CN})_6]_2$ . Insoluble in dilute nitric acid. Soluble in ammonium hydroxide and in potassium cyanide.

**454.** Mercurous nitrate gives a brownish-red precipitate of mercurous ferricyanide.

**455.** Lead solutions give no precipitate.

## FERROCYANIDES.

*Test on Dry Substance.*

**456.** Decomposed when heated to redness.

*Solution Tests.*

**457.** Ferric chloride gives a blue precipitate of ferric ferrocyanide (Prussian blue),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . Insoluble in hydrochloric acid. Decomposed by alkaline hydroxides with separation of ferric hydroxide.

**458.** Copper sulphate gives a reddish-brown precipitate of copper ferrocyanide,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ . Insoluble in dilute acids. Decomposed by alkaline hydroxides.

**459.** Silver nitrate gives a white precipitate of silver ferrocyanide,  $\text{Ag}_4\text{Fe}(\text{CN})_6$ , which slowly turns blue. Soluble in potassium cyanide. Insoluble in ammonium hydroxide and



dilute nitric acid. Decomposed when boiled with ammonium hydroxide.

**460.** Ferrous sulphate gives a white precipitate of potassium ferrous ferrocyanide (if a potassium salt of the acid is present),  $K_2Fe.Fe(CN)_6$ . This precipitate quickly changes in color, becoming blue.

**461.** Lead acetate or nitrate gives a white precipitate of lead ferrocyanide.

**462.** Mercuric chloride gives a white precipitate of mercuric ferrocyanide.

**463.** Zinc sulphate gives a white, gelatinous precipitate of zinc ferrocyanide.

#### CHLORIDES.

##### *Tests on Dry Substance.*

**464.** Sulphuric acid gives hydrochloric acid as a gas, which may be detected by its odor, and the heavy white fumes obtained by holding a glass rod moistened with ammonium hydroxide over the vessel in which the experiment is made. Insoluble chlorides will not give the reaction.

**465.** Manganese dioxide and sulphuric acid and heat, evolve chlorine. Detected by its odor, color, and bleaching action on moist organic coloring matter, as litmus paper, indigo, etc.

##### *Solution Tests.*

**466.** Silver nitrate gives a white precipitate of silver chloride,  $AgCl$ , becoming dark in color on exposure to sunlight. Soluble in ammonium hydroxide, potassium cyanide, strong hydrochloric acid, and concentrated solutions of alkali chlorides. Insoluble in nitric acid.

**467.** Lead acetate gives a white precipitate of lead chloride,  $PbCl_2$ . Soluble in a large amount of cold water, more soluble in hot water; in acetic acid, alkali acetates and thiosulphates. Insoluble in strong alcohol.

**468.** Mercurous nitrate gives a white precipitate of mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ . Soluble in aqua regia and chlorine water. Insoluble in cold dilute acids. Decomposed by alkali hydroxides.

#### CHROMATES.

##### *Tests on Dry Substance.*

**469.** Same as the blowpipe tests for chromium.

##### *Solution Tests.*

**470.** All chromates are colored yellow or red.

**471.** Hydrogen sulphide in the presence of an acid reduces chromates to chromium salts. This change is denoted by the fluid becoming green and sulphur separating. This reducing action is of importance in the separation of the metals, as chromium may be found in the third group which existed as a chromate or a dichromate in the original solution. The reduction to a chromium salt may be brought about by other reducing agents, as tartaric, oxalic and other organic acids; sulphur dioxide, alcohol and zinc.

**472.** Ammonium sulphide produces chromium salts and the separation of chromium hydroxide.

**473.** Barium chloride gives a yellowish-white precipitate of barium chromate,  $\text{BaCrO}_4$ . Soluble in dilute hydrochloric and nitric acids.

**474.** Silver nitrate gives a purplish-red precipitate of silver chromate,  $\text{Ag}_2\text{CrO}_4$ . Soluble in nitric acid and in ammonium hydroxide. In slightly acid solutions, silver dichromate,  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , is formed.

**475.** Lead acetate gives a yellow precipitate of lead chromate,  $\text{PbCrO}_4$ . Soluble in sodium and potassium hydroxides. Slightly soluble in dilute nitric acid. Insoluble in water and acetic acid.

**476.** Treated with an excess of sulphuric acid and shaken with a solution of hydrogen peroxide in ether, a blue color is produced.

## ARSENITES.

*Tests on Dry Substance.*

**477.** Same as the blowpipe tests for arsenic, see 90-92.

*Solution Tests.*

**478.** Hydrogen sulphide in acid solutions gives a yellow precipitate of arsenious sulphide,  $\text{As}_2\text{S}_3$ .

**479.** Ammonium sulphide followed by hydrochloric acid in excess gives the same precipitate as the preceding.

**480.** Silver nitrate in neutral or slightly alkaline solutions gives a yellow precipitate of silver arsenite,  $\text{Ag}_3\text{AsO}_3$ . Soluble in nitric acid and in ammonium hydroxide. Its solution in ammonium hydroxide gives a precipitate of silver on boiling.

**481.** Copper sulphate gives a yellowish-green precipitate of copper arsenite,  $\text{CuHAsO}_3$ . Soluble in nitric acid and alkali hydroxides. Its solution in alkali hydroxides gives cuprous oxide on boiling.

## ARSENATES.

*Tests on Dry Substance.*

**482.** Same as the blowpipe tests for arsenic, see 90-92.

*Solution Tests.*

**483.** Hydrogen sulphide in acid solutions gives a yellow precipitate of arsenic sulphide,  $\text{As}_2\text{S}_5$ , mixed with arsenious sulphide and sulphur. If mixed first with sulphurous acid and heated and then with hydrogen sulphide, arsenious sulphide is precipitated.

**484.** Ammonium sulphide followed by hydrochloric acid gives a yellow precipitate of arsenic sulphide.

**485.** Silver nitrate gives a reddish-brown precipitate of silver arsenate,  $\text{Ag}_3\text{AsO}_4$ . Soluble in nitric acid and in ammonium hydroxide. The solution in ammonium hydroxide does not give a precipitate when boiled.

**486.** Copper sulphate gives a greenish-blue precipitate of copper arsenate,  $\text{CuHAsO}_4$ . Soluble in excess of an alkali hydroxide and in nitric acid. Boiling the solution in excess of hydroxide does not give cuprous oxide.

**487.** Magnesia mixture gives a white precipitate of magnesium ammonium arsenate,  $\text{MgNH}_4\text{AsO}_4$ .

**488.** Molybdic acid in nitric acid gives a fine yellow precipitate on warming or boiling, provided the molybdic solution is in large excess. Precipitate is soluble in ammonium hydroxide, and the arsenic is reprecipitated from this solution with magnesia mixture as magnesium ammonium arsenate.

## PHOSPHATES.

### *Solution Tests.*

**489.** Barium chloride gives a white precipitate of barium phosphate,  $\text{BaHPO}_4$ . Soluble in nitric, hydrochloric, and acetic acids; slightly so in ammonium chloride.

**490.** Calcium sulphate or chloride gives a white precipitate of calcium phosphate,  $\text{CaHPO}_4$ . Soluble in acids and in ammonium chloride.

**491.** Silver nitrate gives a light yellow precipitate of silver phosphate,  $\text{Ag}_3\text{PO}_4$ . Soluble in nitric acid and in ammonium hydroxide.

**492.** Ferric chloride added to a fluid containing but little free acid and plenty of sodium acetate gives a whitish precipitate of ferric phosphate,  $\text{FePO}_4$ . Soluble in excess of ferric chloride.

**493.** Magnesium sulphate gives a white precipitate of magnesium phosphate,  $\text{MgHPO}_4$ . Soluble in acids.

**494.** Magnesia mixture gives a fine, white, crystalline precipitate of magnesium ammonium phosphate. Soluble in acids. Insoluble in ammonium hydroxide. Precipitation assisted by stirring and shaking.

**495.** Molybdic acid in nitric acid gives a fine yellow precipitate, in the cold or on gently heating, provided the reagent

is in large excess. Soluble in ammonium hydroxide and precipitated from this solution by magnesia mixture as magnesium ammonium phosphate.

**496.** Uranic nitrate gives a yellow precipitate of uranic phosphate. Insoluble in acetic acid.

#### SULPHATES.

##### *Test on Dry Substance.*

**497.** Heated on charcoal with pure sodium carbonate, are changed into sulphides. If the fused mass is placed on a bright piece of silver and moistened with water, on removing the mass after a few minutes, the metal will be found colored black from the formation of silver sulphide.

##### *Solution Tests.*

**498.** Barium chloride gives a white precipitate of barium sulphate,  $\text{BaSO}_4$ . Insoluble in acids.

**499.** Lead acetate gives a white precipitate of lead sulphate,  $\text{PbSO}_4$ . Soluble in hot solutions of hydrochloric acid, ammonium acetate, and ammonium tartrate. Slightly soluble in dilute nitric acid. Insoluble in alcohol and dilute sulphuric acid.

#### OXALATES.

##### *Tests on Dry Substance.*

**500.** Mixed with manganese dioxide, moistened with water, and afterwards with a few drops of sulphuric acid, evolve carbon dioxide. Test is best made in a watch glass holding over it another watch glass moistened with lime water. Manganese dioxide used must not contain any carbonate.

**501.** All oxalates are decomposed when heated to redness.

##### *Solution Tests.*

**502.** Barium chloride gives a white precipitate of barium oxalate,  $\text{BaC}_2\text{O}_4$ . Soluble in nitric and hydrochloric acids. Insoluble in acetic and oxalic acids unless just precipitated.

**503.** Calcium chloride gives a white precipitate of calcium oxalate,  $\text{CaC}_2\text{O}_4$ . Soluble in nitric and hydrochloric acids. Insoluble in acetic and oxalic acids.

**504.** Calcium hydroxide gives the same precipitate as the preceding.

**505.** Calcium sulphate also gives the same precipitate.

**506.** Silver nitrate gives a white precipitate of silver oxalate,  $\text{Ag}_2\text{C}_2\text{O}_4$ . Slightly soluble in water, more so in dilute nitric acid, readily soluble in hot nitric acid and in ammonium hydroxide.

#### TARTRATES.

##### *Test on Dry Substance.*

**507.** Heated on charcoal or platinum foil, preferably the latter, carbonization and the odor of burning sugar or grapes are obtained.

##### *Solution Tests.*

**508.** Potassium acetate and other potassium salts in the presence of acetic acid give a white, crystalline precipitate of potassium acid tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ . Precipitation assisted by stirring or shaking. Soluble in alkali hydroxides and in acids. Perceptibly soluble in water. Tartaric and acetic acids do not increase its solubility in water. In the presence of borates, potassium fluoride and not the acetate must be employed in making the test, as borates form a soluble compound with potassium tartrate in the presence of acetic acid.

**509.** Calcium chloride added in excess to neutral solutions gives a white precipitate of calcium tartrate,  $\text{CaC}_4\text{H}_4\text{O}_6$ . Soluble in alkali hydroxides and in acids. Precipitation retarded by the presence of ammonium salts, assisted by stirring and shaking.

**510.** Calcium hydroxide gives the same precipitate as the preceding.

**511.** Barium chloride gives a white precipitate of barium tartrate,  $\text{BaC}_4\text{H}_4\text{O}_6$ . Soluble in acids.

**512.** Lead acetate gives a white precipitate of lead tartrate,  $\text{PbC}_4\text{H}_4\text{O}_6$ . Soluble in nitric acid and in ammonium hydroxide.

**513.** Silver nitrate added to a neutral solution gives a white precipitate of silver tartrate,  $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ . On adding ammonium hydroxide to the fluid containing the precipitate until the latter is almost dissolved and then heating, a mirror of metallic silver forms on the inside of the tube.

**514.** A solution of resorcinol in dilute sulphuric acid and about twenty times its volume of strong sulphuric acid will produce, with a few drops of the fluid containing a tartrate, a violet-red color when warmed.

#### CITRATES.

##### *Test on Dry Substance.*

**515.** Heated on charcoal, carbonization and an acrid odor are obtained; differs from the corresponding test for tartrates.

##### *Solution Tests.*

**516.** Calcium chloride in excess in neutral solutions gives a white precipitate of calcium citrate,  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ . Soluble in alkali citrates and in ammonium chloride. From the last solution it is again precipitated on boiling unless too much chloride is present. A solution of a citrate mixed with calcium chloride in excess, and then with ammonium hydroxide in excess, gives no precipitate until it is boiled.

**517.** Calcium hydroxide added in excess gives no precipitate in the cold; on boiling, calcium citrate separates and dissolves again on cooling.

**518.** Lead acetate gives a white precipitate of lead citrate,  $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ . Soluble in ammonium hydroxide.

**519.** Silver nitrate in neutral solutions gives a white precipitate of silver citrate,  $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$ . On boiling with a little water, this compound is decomposed, and silver is deposited. Will not however give a mirror like silver tartrate.

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## CHAPTER XIII.

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### DETECTION OF THE ACID RADICALS OR ACIDS.

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**520.** In the separation of the metals, certain ones were isolated in groups by the addition of reagents, and each group was taken up in turn and the individual members detected either by separating one from all others of the group, or else by adding a reagent or applying a test which would give a characteristic and conclusive result for one metal in the presence of other metals of the group.

**521.** With the acids or acid radicals, a similar scheme of separation cannot be followed. They can be divided into groups according to their reactions with reagents, but no method can be successfully used for the detection of the individual members of a group by first precipitating a group and then working upon this group precipitate for the isolation of its constituents. For this reason, the acids or acid radicals are detected more by the application of detached tests than by any systematic grouping.

**522.** A careful, practical study of the special tests for the acids will be of great advantage. A familiarity with the individual reactions of each acid is necessary before the student can hope for any success in testing mixtures containing two or more of the radicals.

**523.** A determination of the metals present will often simplify the tests for the acids, as the presence of a certain metal or metals will sometimes prove the absence of one or more acids.

This being especially true when working upon solutions or powders soluble in water.

The method of procedure for their detection is as follows :

#### TESTS ON THE DRY MATERIAL.

**524.** If a fluid is to be examined, a portion of it is very carefully evaporated to dryness, best on a water-bath, and parts of the dry residue used for each experiment, paragraphs **525-531**.

**525.** Heat in a dry test-tube, decomposition with the evolution of a gas which takes fire in the tube and burns from the bottom of the vessel up, together with a garlic-like odor, indicates *hypophosphites*.

**526.** Heat on charcoal with the blowpipe flame.

(a.) Deflagration indicates nitrites, nitrates\* or chlorates, or any combination of these. If substance does not deflagrate, these are absent.

(b.) Carbonization indicates organic acids. (Tartrates citrates, and sometimes acetates).

(a-1.) If the substance deflagrates on charcoal, put a little of the dry material upon the surface of a few drops of sulphuric acid in a watch-glass. A yellow color and a chlorous odor indicate *chlorates*. Test interfered with by the presence of bromides and iodides. If these are present test for chlorates according to paragraph **544**.

(a-2.) If the substance deflagrates, put a little of it into a test-tube, add sulphuric acid and then pour upon the top of the mixture a strong solution of ferrous sulphate. A dark brown or purplish ring at the junction of the two fluids indicates *nitrites* or *nitrates*. Test interfered with by the presence of

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\*. If nitrates are not found by test on dry material and if the original solution is acid, the test with ferrous sulphate and sulphuric acid should be applied to some of the fluid concentrated. The solution may contain free nitric acid which would be driven off in the evaporation to dryness.

chlorates, bromides, iodides, and chromates. If these are present, test according to paragraphs **546, 547, 548.**

(a-3.) To prove the presence of a *nitrite*, a small quantity of the powder is treated with dilute sulphuric acid, effervescence with the liberation of a gas which, in the tube, has a brownish color and a characteristic odor indicates *nitrites*.

**527.** Put a small quantity of the substance into a test-tube and pour upon it dilute sulphuric acid (1 to 5).\* Note whether effervescence takes place and if a gas is generated having an odor, or a color, or both.

(a.) Effervescence and odor of hydrogen sulphide, indicate *sulphides*. If in doubt regarding the odor, hold over the tube filter paper moistened with a solution of lead acetate, a brown to brown-black color on the paper shows the presence of *sulphides*.

(b.) Effervescence and odor of burning sulphur (sulphur dioxide) indicate *sulphites*.

(c.) Effervescence and odor of hydrocyanic acid indicate *cyanides*. In the absence of ferrocyanides and ferricyanides, the test with ferrous sulphate, ferric chloride, &c., can be applied. See special tests for cyanides, paragraph **398.**

(d.) Effervescence and no odor indicate *carbonates*. Confirm by passing some of the gas through lime water, formation of a white precipitate is due to carbonates. In any case where effervescence is obtained, the test with lime water should be made as a carbonate may be present together with one or more of those acids which give an odor when treated with the dilute sulphuric acid.

(e.) Effervescence and liberation of a gas having a brownish color in the tube and the odor of nitrogen dioxide, indicate *nitrites*. See paragraph **526, a-2.**

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\* Dilute hydrochloric acid can be employed in place of the sulphuric acid, but the diluted acid must be free from odor.

(*f.*) Mixture turning yellow and the evolution of a gas having a chlorous odor, indicate *chlorates*. See paragraph 526, a-1.

(*g.*) Liberation of sulphur dioxide, recognized by its odor; and the fluid becoming milky after standing for a short time, indicate *thiosulphates*. Confirm by adding to a neutral solution of the substance ferric chloride; thiosulphates produce a reddish-violet color.\*

**528.** Mix some of the substance in a watch-glass with sufficient sulphuric acid to make a thick mass. Test a part of the mixture in a blowpipe flame on a platinum wire which has been moistened with strong glycerine. A flame having a leaf-green border indicates *borates*. If copper or barium or both have been found in testing for the metals, this test cannot be relied upon for borates. The copper or barium must be removed. This can be done by boiling with an excess of sodium carbonate, filtering and evaporating the filtrate down to small bulk and then applying the test as above.

**529.** Put some of the substance into a test-tube and add a few drops of alcohol to it, then pour in a moderate excess of sulphuric acid and warm. An odor of acetic ether indicates *acetates*.† If chlorates have been found extreme care must be taken in adding the sulphuric acid. Before any reliance can be placed on this odor test, the student must be familiar with the odor of the substance formed, acetic ether, as other ethers are produced in the presence of certain acids and the beginner is apt to mistake one of these for acetic ether.

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\* If the substance under examination contains more than one of the acids which decompose (when treated with dilute sulphuric acid) with the liberation of gases having odors; it may be necessary to resort to one or more of the separations described in paragraphs 549-556.

† If the original solution contains free acetic acid, this would be expelled during the evaporation of it to dryness. In this case acetates might not be detected by testing as per paragraph 529. During the evaporation, however, the odor of the acid would be noted.

**530.** Mix some of the substance with sulphuric acid in a watch-glass and set it aside for about ten minutes. Wash out the mixture with water and note if the surface of the glass has been roughened where the mixture was in contact with it. The effect is best seen by drying the glass and then breathing upon it. Such roughening indicates *fluorides*.

**531.** Mix the substance with enough nitric acid to make it acid and then thoroughly dry it. To the residue add nitric acid again, warm, and dilute with water. Filter and test insoluble, if any, in a sodium metaphosphate bead; an insoluble skeleton of silica indicates *silicates*.

#### TESTS ON SOLUTION.

**532.** Add to a solution of the substance sodium carbonate in excess and boil for some minutes. Filter and test insoluble, if any, for silicates, fluorides, and phosphates. Reserve the filtrate and use parts of it for the following tests, paragraphs **533-543**.

**533.** To a portion of the filtrate add nitric acid until just acid and then silver nitrate in excess and filter. A precipitate proves the presence of *chlorides*, *bromides*, *iodides*, *cyanides*, *ferrocyanides*, *ferricyanides*, or *sulphides*, or any combination of these; and sometimes *oxalates*, *hypophosphites*, and *thiosulphates*. If the precipitate formed is absolutely white in color, it shows that chlorides, cyanides, ferrocyanides, and perhaps oxalates are present while the other members of the set are absent as they give colored precipitates. If the silver nitrate does not produce a precipitate, *chlorides*, *bromides*, *iodides*, *cyanides*, *ferrocyanides*, *ferricyanides*, and *sulphides* are not present, and no other tests need be made for them. In either case after adding silver nitrate in excess, carefully pour on the filtrate dilute ammonium hydroxide (1 to 2) so that it floats on the fluid in the tube. A ring at the junction of the two indicates *arsenites*, *arsenates*, *chromates*, *phosphates*, *oxalates*, *nitrites*, *sulphites*. Note color of the ring. Arsenites and phosphates give a yellow ring; arsenates, a reddish-brown; chromates, a purplish-red; and the others, white.

The following tests, paragraphs **534-537**, are made provided a precipitate has been obtained by silver nitrate.

**534.** Add to a portion of the filtrate obtained by boiling with sodium carbonate and filtering, hydrochloric acid until acid, some carbon disulphide and finally a solution of sodium hypochlorite. The last mentioned must be added carefully, a drop or two at a time, keeping the fluid *acid* with hydrochloric acid throughout the operation, and mixing well as the reagent is dropped in. A violet color imparted to the carbon disulphide indicates *iodides*, a yellow-brown to a red color indicates *bromides*. If the mixture contains both iodides and bromides, the violet color will first appear; by adding the sodium hypochlorite in small quantities as described above, mixing well between each addition, and keeping the fluid acid, the violet color due to the iodine will disappear and will be replaced by the yellow-brown or red of bromine. Test interfered with by the presence of cyanides, ferrocyanides, and ferricyanides. See paragraph **560**.

**535.** Add excess of hydrochloric acid and then ferrous sulphate, a blue precipitate indicates *ferricyanides*.

**536.** Add excess of hydrochloric acid and then ferric chloride, a dark blue precipitate indicates *ferrocyanides*.

**537.** Add nitric acid in excess and then silver nitrate, a white precipitate, soluble in ammonium hydroxide, indicates *chlorides*. Test interfered with by the presence of sulphides, cyanides, ferrocyanides, ferricyanides, bromides and iodides. Also by thiosulphates and hypophosphites.

Test for chlorides in presence of sulphides, see paragraph **558**. In presence of cyanides, ferrocyanides, or ferricyanides, see paragraph **560**. In presence of iodides and bromides, see paragraph **559**. In presence of thiosulphates and hypophosphites, see paragraph **560**.

**538.** If the solution is yellow add acetic acid in excess and then lead acetate. A yellow precipitate, soluble in sodium hydroxide, indicates *chromates*, see paragraph **561**.

**539.** If arsenic is found in testing for the metals, arsenites and arsenates must be looked for among the acids. The color of the ring obtained by pouring ammonium hydroxide on the filtrate after making acid with nitric acid, adding silver nitrate in excess, and filtering, will show the presence of an arsenite or arsenate if phosphates and chromates are absent. A yellow ring indicates *arsenites*. A reddish-brown ring, *arsenates*. Detection of these two radicals in presence of phosphates and chromates, see paragraphs **562, 563, 564**.

**540.** Add nitric acid in excess and mix a few drops of this fluid with molybdic solution and warm. A yellow precipitate indicates *phosphates*. If *arsenic* is found in testing for the metals it must be removed before applying the above test for phosphates, as arsenates give with molybdic solution a precipitate having the same color as phosphates. The best method to remove the arsenic is to make a part of the fluid used for the tests for acid radicals, acid with hydrochloric acid, heat to about the boiling point and pass through it hydrogen sulphide, continuing the passing of the gas for about five minutes and keeping the fluid hot. This will precipitate from the solution all of the arsenic. The precipitate is filtered off, a few drops of nitric acid added to the filtrate and the mixture boiled to decompose the hydrogen sulphide. Filter, if necessary, and add a few drops of this fluid to some molybdic solution and warm. A yellow precipitate indicates *phosphates*.

**541.** Add hydrochloric acid in excess and then barium chloride. A white precipitate indicates *sulphates*.

**542.** Add acetic acid in excess and then calcium sulphate solution. A white and finely divided precipitate indicates *oxalates*.

**543.\*** Add acetic acid until the fluid is slightly acid, bring up to the boiling point, and add to the boiling fluid calcium

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\* Tartrates and citrates need not be tested for unless the substance charred, paragraph 526 b.



chloride in excess (until it produces no more precipitate) and filter. Make filtrate slightly alkaline with ammonium hydroxide, cool and filter again; save precipitate and filtrate. Wash precipitate with water, transfer to a test tube, add a moderate excess of silver nitrate and four or five drops of ammonium hydroxide and heat. A coating or mirror of silver on the sides of the tube indicates *tartrates*. The filtrate obtained by adding ammonium hydroxide until slightly alkaline, cooling and filtering, is slowly boiled for some time, if a precipitate does not form add a little more calcium chloride and ammonium hydroxide and boil again. A precipitate which chars when heated, insoluble in cold potassium hydroxide, and soluble in a neutral solution of cupric chloride, indicates *citrates*.

## CHAPTER XIV.

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### SEPARATION AND DETECTION OF INTERFERING ACID RADICALS OR ACIDS.

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**544.** Detection of *chlorates* in the presence of *bromides* and *iodides*. Add to solution containing the acids, made acid with nitric acid, silver nitrate in slight excess, filter and evaporate to dryness and ignite. Dissolve in water, make acid with nitric acid and add silver nitrate; a white precipitate indicates *chlorates*.

**545.** — *Chlorates* in the presence of large amounts of *nitrates* and *nitrites*. Add to a solution of the substance, nitric acid until the fluid is acid, and then silver nitrate in slight excess. Filter, evaporate to dryness and ignite. Dissolve residue in water, make acid with nitric acid and add silver nitrate. A white precipitate indicates *chlorates*.

**546.** Detection of *nitrates* in the presence of *chlorates*. Ignite with sodium carbonate, and test with sulphuric acid and ferrous sulphate.

**547.** — *Nitrates* in the presence of *bromides* and *iodides*. Add to solution, silver sulphate in excess, filter, and evaporate filtrate carefully to dryness and test with sulphuric acid and ferrous sulphate.

**548.** — *Nitrates* in the presence of *chromates*. Make solution slightly acid with sulphuric acid and add some sodium sulphite; then make alkaline with ammonium hydroxide, filter, evaporate the filtrate carefully to dryness, and test with sulphuric acid and ferrous sulphate.

**549.** Detection of *thiosulphates* in the presence of *sulphites*. Add to a neutral solution of the substance, ferric chloride. A reddish-violet color proves *thiosulphates*.

**550.** — *Thiosulphates* in the presence of *sulphides*. Precipitate the sulphides, best in neutral solution, by adding a solution of zinc sulphate in excess, filter and test filtrate for *thiosulphates*.

**551.** — *Thiosulphates* in the presence of *cyanides*. Add to a water solution, zinc sulphate in excess, filter and wash. Test the precipitate for *cyanides* and the filtrate for *thiosulphates*.

**552.** Detection of *sulphites* and *thiosulphates* in the presence of *sulphides*. Add to a water solution of the substance zinc sulphate in excess. This will precipitate the sulphide while the other two remain in solution. The sulphide of zinc is filtered off and the filtrate divided into two parts. One part is tested for *thiosulphates* with dilute sulphuric acid, giving sulphur dioxide and precipitated sulphur; the other part is tested for *sulphites* by making slightly acid with acetic acid and adding a small amount of sodium nitroprusside, according to paragraph **555**.

**553.** Detection of *sulphites* in the presence of *sulphides*. Add to a water solution, zinc sulphate in excess, filter and wash precipitate. Test the precipitate for *sulphides* and the filtrate for *sulphites*.

**554.** — *Sulphites* in the presence of *cyanides*. Add to a water solution, calcium chloride in excess. This will precipitate the larger part of the sulphite while the cyanide will remain in solution. After filtering test the precipitate with dilute acid for *sulphites*, and the filtrate for *cyanides* either with dilute acid or else, in the absence of ferrocyanides or ferricyanides, according to paragraph **398**.

**555.** — *Sulphites* in the presence of *thiosulphates*. To a water solution of the substance add acetic acid until slightly acid, then add to a relatively large amount of a solution of zinc sul-

phate mixed with a small quantity of sodium nitroprusside ; the fluid acquires a red color if the quantity of sulphite is not too small. If very small, the coloration only makes its appearance after adding a solution of potassium ferrocyanide. Sometimes after adding this substance, a purplish-red precipitate will form.

**556.** Detection of *sulphides* in the presence of *cyanides*. Add to a water solution, manganese sulphate in excess, this will precipitate the sulphides. Filter, and after washing, test the precipitate for *sulphides* and the filtrate for *cyanides*.

**557.** Detection of *cyanides* in the presence of *ferro-* and *ferricyanides*. Add to a water solution, manganese sulphate in excess and filter. Make filtrate alkaline with ammonium hydroxide and filter again. This treatment removes entirely the interfering ferro- and ferricyanides, and the filtrate, after making it acid with hydrochloric acid, can be tested for cyanides by adding a solution of ferrous sulphate, a few drops of ferric chloride, then sodium hydroxide in excess, warming, and finally making acid with hydrochloric acid. A blue precipitate proves the presence of *cyanides*.

**558.** Detection of *chlorides* in the presence of *sulphides*. Make the solution acid with nitric acid and boil until sulphides are decomposed, filter if necessary and add silver nitrate, a white precipitate, soluble in ammonium hydroxide, indicates *chlorides*.

**559.** — *Chlorides* in the presence of *iodides* and *bromides*. Make the solution acid with sulphuric acid, add a strong solution of ferric alum (ferric ammonium sulphate) and boil. This liberates the iodine and the boiling should be continued until no more vapors of iodine are observed coming from the tube. Now add a solution of potassium permanganate in quantity sufficient to impart its color to the fluid and boil again. If the color of the permanganate disappears, add enough more to color the fluid and boil again. Continue the addition of the permanganate and the boiling, until after boiling for a short time the fluid retains a violet or purple color. The solution is filtered and the remaining potassium permanganate decomposed by add-

ing a few drops of alcohol, warming, and filtering again. The filtrate is now made acid with nitric acid and silver nitrate added. A white precipitate, soluble in ammonium hydroxide, indicates *chlorides*.

**560.** Detection of *chlorides*, *bromides* and *iodides* in the presence of *cyanides*, *ferrocyanides*, *ferricyanides*, *thiosulphates*, and *hypophosphites*. This is best done by decomposing the interfering bodies by first precipitating as silver salts with silver nitrate, filtering, drying, and igniting. The ignited residue is mixed with sodium carbonate and fused, the fusion is extracted with water and filtered, and the filtrate tested according to paragraph **534**, for *bromides* and *iodides* and paragraph **559** for *chlorides*.

**561.** If *chromium* is found in testing for the metals in the regular separation, it is necessary to determine whether it exists as a base or as an acid radical in the original. Chromates and dichromates are reduced by hydrogen sulphide and by ammonium sulphide to chromium salts, and chromium will be found in the third group, although it does not exist as a chromium salt in the original. On this account a portion of the precipitate obtained by boiling with sodium carbonate for the acids is dissolved and tested for chromium. If found by this testing, it proves the presence of chromium as a base.

**562.** Detection of *arsenites* and *arsenates* in the presence of *chromates*. Make the solution acid with acetic acid and add barium acetate in excess, filter, and to the filtrate add silver nitrate in excess. Brown precipitate indicates *arsenates*, yellow precipitate, *arsenites*. If the precipitate is brown, proving the presence of arsenates, dissolve it in ammonium hydroxide and boil, a mirror of metallic silver indicates *arsenites*. If sulphides, chlorides, cyanides, bromides, &c., are present, they must be removed after adding the barium acetate in excess and filtering, before the tests for arsenites and arsenates can be made.

**563.** Detection of *arsenites* in the presence of *phosphates*. Add to a neutral solution, silver nitrate in excess and filter.

Dissolve the precipitate in a small amount of ammonium hydroxide and boil, a precipitate or mirror of metallic silver indicates *arsenites*.

**564.** — *Arsenites* in the presence of *arsenates*. Add silver nitrate, filter, &c., as in the previous separation. A precipitate or mirror of metallic silver indicates *arsenites*.

If tartrates or citrates or both are present they must be removed as they have a reducing action upon the silver compounds. Their removal is best accomplished in the form of calcium salts.

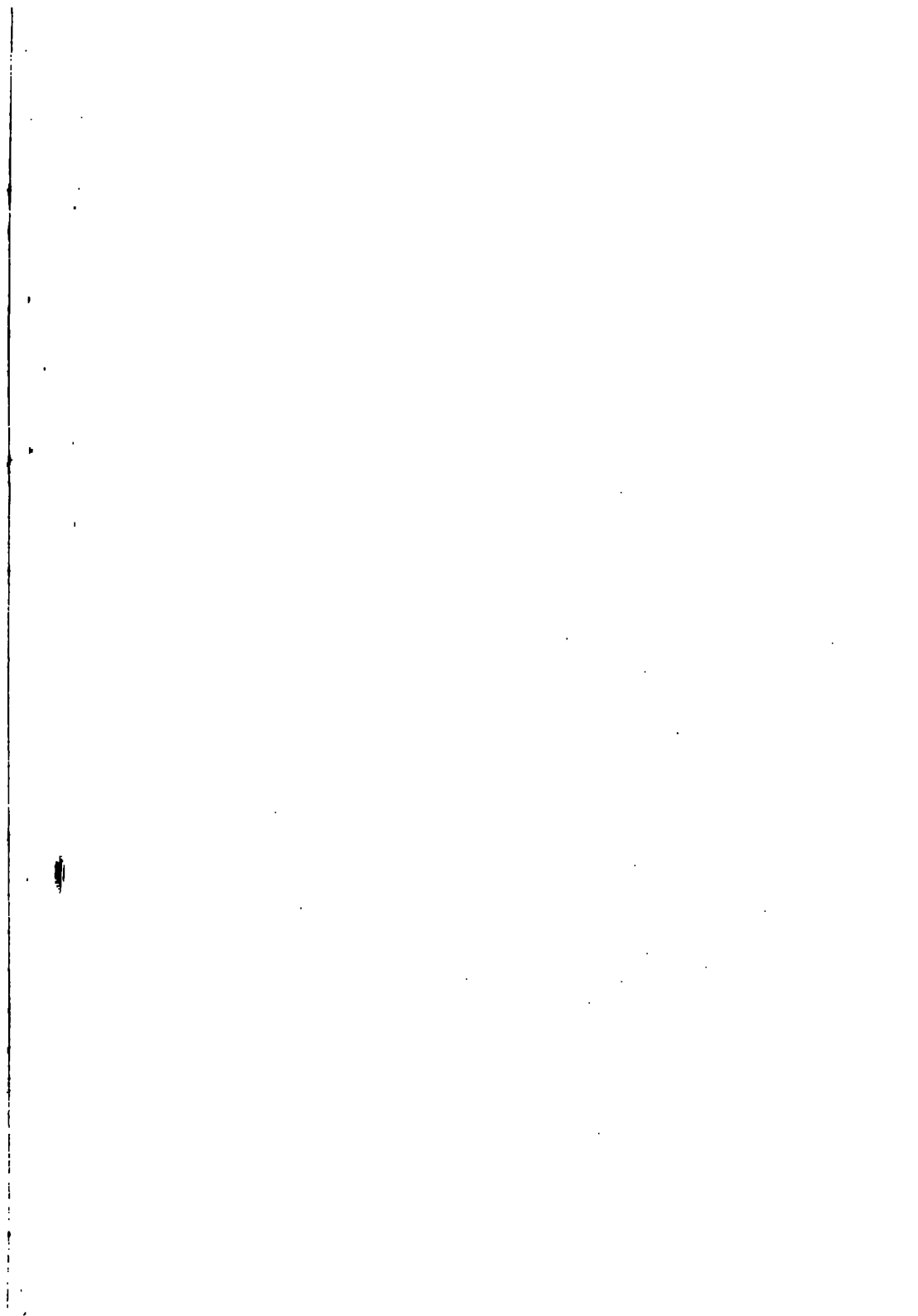
**565.** Detection of *sulphates*, *sulphites*, and *thiosulphates* in the presence of each other. A dilute solution containing the salts is mixed with barium and ammonium chlorides in excess. Hydrochloric acid is then added, drop, by drop until it is evident that all the barium sulphite and thiosulphate are dissolved. The solution is then filtered, the filtrate should be perfectly clear. If it becomes opaque, it must be rejected, and a more dilute one started with. To half the filtrate, iodine solution is added until it imparts a permanent yellow tinge, a white precipitate indicates a *sulphite* which the iodine has oxidized to a sulphate forming the barium salt. The two halves are then mixed and more iodine added if necessary, and filtered clear. Half of this fluid is then taken and mixed with bromine water, a white precipitate indicates *thiosulphate*. The thiosulphate is oxidized by the iodine to tetrathionate, and this by the bromine to sulphate, forming barium sulphate. The presence of hydrogen sulphide interferes with the separation. (R. Greig Smith.)

**566.** Detection of *tartrates* in *citrates*. One gramme of citric acid is added to 1 c. c. of ammonium molybdate (10%) and 2-3 drops of hydrogen peroxide ( $\frac{1}{4}$ -1½%), and is heated at 100° for 3 minutes. A fine blue color indicates *tartrates*.









## CHAPTER XV.

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### TREATMENT OF MIXTURES CONTAINING COMPOUNDS INSOLUBLE IN WATER.

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**567.** The character of the solution used to make the analysis will often determine the presence or absence of certain metals or acid radicals. For example, lead and sulphuric acid or barium and sulphuric acid cannot exist in any water solution, since both these combinations are insoluble in water. It is therefore quite necessary to ascertain if the solution is acid, alkaline or neutral when starting an analysis. The beginner should acquire the habit of testing a fluid given to him in order to determine this point at once.

**568.** Another important point to be remembered is the fact that in acid solutions too much acid may interfere with the use of hydrogen sulphide, and if the solution is acid with nitric acid this will require much more dilution than in the case of hydrochloric acid. Here again we may get an indication of the presence of two metals in a solution from its behavior on dilution. If the addition of water to an acid solution gives a milky precipitate, the presence of bismuth or antimony may be suspected.

**569.** When the substance to be analyzed is a solid, or a solution containing a precipitate, it is treated with various liquids to ascertain which is the best solvent for it. The solid is best acted upon by first reducing it to a very fine powder if possible; and in the case of a solution containing a precipitate, the precipitate is filtered off and thoroughly washed with cold water to remove adhering salts in solution.

**570.** As water is the best solvent as far as the method of analysis is concerned, this in a heated condition is always used first. A small quantity of the insoluble is treated with boiling water, if it dissolves, a larger quantity is treated in the same way and the solution can be used immediately for analysis.

**571.** If the solid does not dissolve in hot water, take another small portion and heat it with hydrochloric acid, add a small quantity of water (3 to 4 times the volume) and heat again. Certain compounds will dissolve in the hot concentrated acid, but will separate out again in an insoluble form on diluting. If such separation occurs, add a few drops more of the acid and warm again, and if the solution is clear treat a larger amount of the solid in the same way using as small a quantity of hydrochloric acid as will bring about solution. If it is found by this experiment that this acid can be employed as a solvent, dilution with water to the extent of ten volumes is necessary before the fluid can be used in the separation of the metals. Very often this amount of dilution will cause the formation of a precipitate, although everything was dissolved before the addition of the larger amount of water, especially when antimony or bismuth is present. In this case a little more hydrochloric acid and warming will cause the precipitate to dissolve. This solution can be used for testing for all the metals and for all the acids excepting those radicals decomposed by this acid and chlorides. Those decomposed by hydrochloric acid, as the carbonates, sulphides, &c., will be detected when the solid is treated with the acid in the preparation of the solution, or else in their proper place in the analysis according to the acid scheme. To test for chlorides, another portion of the solid is treated with some other solvent, preferably nitric acid which does not interfere, and the test made in the regular way. In the presence of silica, see **580**. If substance dissolved was a precipitate in a solution, see **581**.

**572.** If the solid does not dissolve in hydrochloric acid, take another small portion and heat with nitric acid, add a small quantity of water equal to 3 or 4 times the volume of acid em-

ployed and heat again. If by this treatment perfect solution results, dissolve a larger quantity in the same way. It is advisable to then add hydrochloric acid and to continue the heating until all of the nitric acid has been decomposed, then dilute with water and treat any precipitate which forms for the metals of the first group, the same care being exercised regarding the possible separation of bismuth and antimony as in paragraph **571**. Any mercurous compounds present in the insoluble will, by the nitric acid treatment, be converted into mercuric salts; and mercury instead of being found in the first group, will be detected in the second. However if the original insoluble material is treated with ammonium hydroxide, mercurous compounds will be turned black and can be thus detected. The solution thus prepared by nitric acid and then by the addition of hydrochloric acid can be used not only for the separation of the metals, but also for the majority of the acid radicals which are tested for after boiling with sodium carbonate in excess. Chlorides are tested for as described in paragraph **571**. Organic acids and many bromides and iodides are decomposed by the treatment. The presence of such bromides and iodides will be denoted by the liberation of bromine and iodine during the action of the hot nitric acid. Tartrates and citrates are absent unless the original material chars on heating. Acetates are tested for directly in the original material. Ferrocyanides will be converted into ferricyanides. In the presence of silica, see **580**. If the substance dissolved was a precipitate in a solution, see **581**.

**573.** If the solid does not dissolve in nitric acid, take another small portion and treat it with a mixture of nitric acid, one part; and hydrochloric acid, two parts. Warm gently until chemical action begins and allow it to continue for a few minutes. If solution is affected, dissolve a larger quantity in the same way, evaporate off the excess of acid and dilute with about ten volumes of water. If the addition of water produces a precipitate, the mixture is treated in the manner described in paragraph **571**. The changes occurring when solution is brought about by the nitric acid treatment also take place with aqua regia (decomposition

of bromides, iodides, organic acids, and oxidation of ferrocyanides). The testing for the detection of the metals and those acids determined in the filtrate after boiling with sodium carbonate in excess and filtering, is carried on in the same way as described in paragraph 572. In the presence of silica, see 580. If the substance dissolved was a precipitate in a solution, see 581.

**574.** If hydrochloric acid or aqua regia give complete solution which will bear dilution, it is evident that metals of the first group are absent (except perhaps traces of lead and mercury), since these give insoluble chlorides.

**575.** Substances which are not dissolved by any of the acids tried, or which are only partially dissolved, are best treated as insoluble.

**576.** If silver and lead are present (determined by testing a small portion on charcoal), treat according to paragraphs 577 and 578. If they are absent, according to paragraph 579.

**577.** Boil a portion of the finely powdered substance with several fresh quantities of ammonium acetate and filter. The solution may contain lead chloride or sulphate. To a portion of it add nitric acid in excess and then silver nitrate; a white precipitate, soluble in ammonium hydroxide, indicates *chlorides*. To another portion add hydrochloric acid in excess, filter if necessary, and then add barium chloride; a white precipitate, insoluble in hydrochloric acid, indicates *sulphates*. To a third portion add sulphuric acid in excess, a white precipitate indicates *lead*.

**578.** Wash the material insoluble in ammonium acetate, and warm it with a solution of potassium cyanide, using several fresh portions, and filter. The solution may contain silver chloride, and a little sulphate from barium sulphate (if present) decomposed by potassium carbonate in the potassium cyanide used. To one portion of this fluid add ammonium sulphide, a black precipitate indicates *silver*. Filter out this precipitate and dissolve it in nitric acid, dilute the solution, and add hydrochloric

acid to prove that it contains silver. If silver is present, precipitate another portion of the cyanide solution with ammonium sulphide in excess, to remove all the silver, mix the filtrate with sodium carbonate and evaporate to dryness. The dry residue will contain the *acids*, and may be tested in the ordinary way. Remember there are only a few insoluble silver compounds.

**579.** The material insoluble in potassium cyanide is now washed and dried. Fuse the dry substance insoluble in potassium cyanide with two parts each of a mixture of dry potassium and sodium carbonates and one part of potassium nitrate. When the mixture is melted, allow it to cool, and treat it with water in several portions, boiling the last. The insoluble matter contains the metals (except aluminium) with some silicates, and the solution contains the acid radicals and aluminium. Dissolve the insoluble matter from the fusion in hydrochloric acid, and proceed with this solution as in the ordinary method of analysis. Proceed to test the water solution from the fusion for acids.

**580.** If silica is present in the substance under examination, and a test with a sodium metaphosphate bead will determine this, the fluid obtained by dissolving the substance, must be evaporated to dryness, and residue taken up with the acid used to obtain solution in order to remove the silica, which remains behind in an insoluble form after this treatment. If it is found necessary to fuse the substance, the water extraction of the fused mass is evaporated in the same way, after making it slightly acid with hydrochloric acid, and the residue taken up with hydrochloric acid and water. This acid will not interfere with the tests for the acid radicals, as any chlorides present in the original have been removed and tested for by the previous operations.

**581.** If the material treated was originally a precipitate in a solution and it has been found to dissolve by the action of the solvents, as described in paragraphs **570**, **571**, **572**, or **573**, tests should be made to determine whether the dissolved substance can be mixed with the fluid from which the precipitate was filtered. Such tests should be made by using small quantities

of the fluids in question. If no precipitation takes place on mixing, then the larger quantities can be added to each other and one analysis made for metals and acids. If precipitation occurs, no matter what solvent is employed, then separate determinations of metals and acids must be made in the filtered fluid and in the dissolved precipitate.

## CHAPTER XVI.

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### SPECIAL METHODS.

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#### MODIFICATION OF THE PROCESS FOR GROUPS III AND IV WHEN PHOSPHATES, OXALATES, TARTRATES, AND OR- GANIC MATTER ARE PRESENT.

**582.** The tests for the interfering bodies are best made in the filtrate after separating the second group with hydrogen sulphide. This fluid is boiled to remove the hydrogen sulphide and small portions tested for *phosphates* with nitric acid and molybdic solution; *oxalates*, by heating a concentrated solution with some manganese dioxide (free from carbonate) and a small amount of dilute sulphuric acid, giving an effervescence and carbon dioxide; *tartrates* and *organic matter* by evaporation with sulphuric acid.

**583.** If oxalates, tartrates, or organic matter are present, the balance of the fluid from the second group is evaporated to dryness with nitric acid, and ignited gently. The residue is taken up with hydrochloric acid and water, and boiled, and the separations proceeded with in the ordinary way.

**584.** If phosphates are present, the separation of groups III and IV must be modified to prevent the precipitation of barium, strontium and calcium in the third group. The balance of the filtrate from group II is boiled with a small amount of nitric acid to oxidize any iron that may be present. The fluid is then nearly neutralized with ammonium hydroxide, the addition of the reagent being continued until the precipitate which forms, only dissolves very slowly on mixing. If too much



of the ammonium hydroxide is added and a permanent precipitate is produced, add hydrochloric acid, a drop at a time, until the precipitate just dissolves. Add an excess of ammonium acetate and a small amount of acetic acid. This will in a subsequent operation precipitate the phosphates of iron and possibly aluminium and chromium. If sufficient iron is present to precipitate all the phosphoric acid, the solution after the addition of the ammonium acetate, will have a red color. If it is colorless, add ferric chloride until the red color appears or until a few drops of the liquid give a red precipitate with ammonium hydroxide. Boil for about five minutes, filter hot, and test the filtrate in the usual way for groups III, IV and V. The precipitate filtered off may contain besides iron, aluminium and chromium, and must be tested for the presence of these metals. Dry the precipitate and fuse it with sodium carbonate. Extract the fused mass with hot water, filter and divide filtrate into two parts. Test one part for chromium by making acid with acetic acid and adding lead acetate, and the other part for aluminium by making acid with hydrochloric acid and then alkaline with ammonium hydroxide and boiling.

#### SEPARATION OF NICKEL AND COBALT BY THE NITRITE METHOD.

**585.** The sulphides of these two metals obtained in the separation of group III are dried, scraped off the filter paper and dissolved in a few drops of aqua regia. Evaporate off the excess of acid, dilute the fluid with a little water and add sodium hydroxide till it is very nearly neutralized, but still remains slightly acid. Now add potassium nitrite solution (1 in 2) and acetic acid to strong acid reaction. The amount of nitrite to add is about three times the volume of the solution. After adding the acetic acid, allow the mixture to stand twelve hours. The cobalt separates out as yellow nitrite of cobalt and potassium. Filter out the precipitate and add sodium hydroxide to the filtrate. A green precipitate, giving a brown bead with borax, proves the presence of nickel.

## SEPARATION OF LEAD, MERCURY, BISMUTH, COPPER AND CADMIUM.

**586.** The precipitate of the second group, after washing with water, is treated with dilute ammonium sulphide, warmed, and filtered. The solution contains arsenic, antimony, and tin; the insoluble, lead, mercury, bismuth, copper, and cadmium. The insoluble is washed with water and treated as follows:

**587.** Dry the washed insoluble by placing the filter paper, unfolded, over a small gas flame, and at such a distance above it that the paper is not charred. Dry till the precipitate can be readily scraped off the paper with a knife.

**588.** Put the dry material into a porcelain dish and add to it enough aqua regia (1 volume of nitric acid and 2 volumes of hydrochloric acid) to make it thoroughly wet. Do not use more acid than is necessary. Heat the acid mixture very gently until all the dark matter is changed to a yellowish color, which is sulphur, and then continue the heating till only a few drops of fluid remain in the dish. Be very careful not to bake the material in the dish, move the fluid around the sides of the dish as it evaporates, leaving the matter still moist when the work is complete.

**589.** Now add to the contents of the dish a few drops of sulphuric acid and only enough to make the mass perfectly fluid. Heat the dish again till heavy white fumes of sulphuric acid are given off, and then cover it with another dish and allow to cool.

**590.** The preceding steps are taken to turn the sulphides, first into chlorides by aqua regia, and then into sulphates by the sulphuric acid. If the chlorides become overheated during the evaporation of the acid, they may be turned into compounds that will not give sulphates with the sulphuric acid, hence it is important to take the precautions given above.

**591.** After the dish is cool (*it must be cool*) add to the fluid in it enough water to dilute the acid to ten times its volume, and stir well. Allow the insoluble matter to settle, pour the

fluid off into a test tube, and add a few more drops of sulphuric acid, and then ten times its volume of water, to the contents of the dish, and stir well again. By this treatment all the soluble matter will be dissolved out. Pour off the second lot of water into the tube that contains the first portion used, and filter the combined fluids. The insoluble material is lead sulphate, and indicates that this group contains lead not precipitated by hydrochloric acid. This lead sulphate should be a fine, very heavy, white precipitate in the bottom of the dish; but if the dry precipitate of sulphides insoluble in ammonium sulphide, contains any filter paper removed during the scraping, see 587, then it may be dark colored.\*

**592.** The filtered fluid from the lead sulphate now contains the other metals, mercury, bismuth, copper and cadmium, as sulphates.

**593.** Place a few drops of the fluid in a watch glass and put into it a clean piece of copper wire. Allow this to stand for a few minutes, and if a gray deposit forms on the wire, which when rubbed with the finger gives a bright white metallic surface, mercury is present in the group, the deposit being fine globules of mercury precipitated by the copper. Having used copper in the watch glass, throw this fluid away.

**594.** The rest of the solution 592 from which a few drops were taken is next mixed with ammonium hydroxide till it is distinctly alkaline after shaking well. Filter out the precipitate formed and wash it well with three lots of water.

Set the filtrate aside for the present and proceed with the precipitate as follows:

**595.** Dissolve the well washed precipitate off the filter paper with the least possible quantity of hydrochloric acid, using a

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\* In any case to prove the presence of lead, wash the residue in the dish, by mixing with water, allow to settle, pour off the water and add to the insoluble matter, forty or fifty drops of sodium or potassium hydroxide, warm and then make acid with acetic acid. Filter if necessary and add to the fluid a few drops of potassium dichromate. A yellow precipitate is lead chromate and proves the presence of lead.

few drops. Boil down the acid fluid till only enough remains in the test tube to allow one or two drops to be poured out. Pour these drops into a tube full of cold water. If a fine white cloud forms after some minutes, it is bismuth oxychloride, and indicates the presence of bismuth.

**596.** The precipitate formed by ammonium hydroxide may be a compound of mercury together with bismuth hydroxide. The solution in hydrochloric acid converts both these into chlorides; the bismuth chloride gives an insoluble oxychloride with water, while the mercury chloride is left in the solution, hence the above treatment serves to distinguish them. Care must be taken that the fluid poured into the water does not contain too great an excess of acid, and this is the reason for boiling the fluid down to a few drops.

**597.** Now return to the filtrate from the ammonium hydroxide precipitate (see **594**). This contains the copper and cadmium. If it has a blue color, copper is present in this group. In order to find cadmium in this fluid, proceed as follows:

**598.** To the solution add acetic acid till the fluid is acid to test-paper. Pass through the fluid hydrogen sulphide until it is saturated, and filter out the precipitate formed. This precipitate contains both copper and cadmium as sulphides. The filtrate from these is thrown away. If the precipitate with hydrogen sulphide is yellow, cadmium is present.

**599.** The mixed sulphides of copper and cadmium are washed on the filter as usual, the filter is pierced with a glass rod and the precipitate is washed into a test-tube with dilute sulphuric acid (1 in 6), and the mixture is boiled for some minutes. By this treatment the cadmium sulphide dissolves while the copper sulphide remains. Filter out the copper sulphide, and it may be thrown away. The matter insoluble in sulphuric acid may also be mercuric sulphide if that metal has already been found. Copper is not present unless it has given a blue color with ammonium hydroxide. To the solution add ammonium hydroxide till the fluid is just alkaline, then add hv

acid, drop by drop, till the fluid is just acid. Cool the fluid and pass hydrogen sulphide through it until it is saturated. If a yellow precipitate forms, it is cadmium sulphide, and indicates the presence of cadmium.

**600.** The reasons for the last steps are: Sulphuric acid has the property of dissolving cadmium sulphide, and if it is not too strong it will not dissolve copper sulphide; it is therefore important to dilute the acid as above. The acid fluid containing the cadmium cannot readily be precipitated by hydrogen sulphide, and the acid has to be neutralized by ammonium hydroxide; then a few drops of hydrochloric acid bring it into the proper condition for the use of hydrogen sulphide. Cadmium sulphide is insoluble in weak hydrochloric acid.

#### SEPARATION OF ARSENIC, ANTIMONY AND TIN BY FUSION METHOD:

**601.** The dried sulphides from the ammonium sulphide solution of the second group are ground with a mixture of one part of sodium carbonate and three parts of sodium nitrate. This mixture is fused at as low a temperature as possible in a porcelain crucible. The fused mass when cold is treated with cold water, which dissolves the arsenic as sodium arsenate, while the tin and antimony are in the insoluble matter. This latter is washed with dilute alcohol (one of alcohol and three of water) put into a dish with zinc and hydrochloric acid and tested in the ordinary manner. The solution of the fusion is made acid with nitric acid and silver nitrate added. If a precipitate is formed, filter it out, and to the filtrate add dilute ammonium hydroxide (one of solution with ten of water) inclining the tube so that the fluid floats on the filtrate. At the junction of the two liquids a reddish-brown precipitate of silver arsenate is formed if arsenic is present.

#### SEPARATION OF ARSENIC, ANTIMONY AND TIN BY THE ACTION OF NASCENT HYDROGEN.

**602.** After treating the precipitate of the second group with warm dilute ammonium sulphide and filtering, the fluid is made

## H<sub>2</sub>S Group.

<p><b>Insoluble.</b>—Drain and dry. Dissolve all (except S) in Aqua Regia (1 HNO<sub>3</sub>, 2 HCl) using only a few drops. Boil off excess of acid, <i>but do not dry</i>. Add a few drops of H<sub>2</sub>SO<sub>4</sub>, heat till white fumes appear, <i>cool</i>, add water, stir well and filter, repeat treatment with acid and water.</p>	<p>Add dilute (NH<sub>4</sub>)<sub>2</sub>S, shake well, warm, filter and wash.</p>	<p><b>Filtrate.</b>—Contains As, Sb, and Sn.</p>
<p><b>Residue</b> is PbSO<sub>4</sub> and indicates <b>Pb</b>.</p>	<p><b>Filtrate.</b>—Divide in two parts.</p>	
<p>I.—<i>Small</i> in W. G. Add clean Cu wire. Metallic coat is <b>Hg</b>.</p>	<p>II.—<i>Large</i>. Add NH<sub>4</sub>OH in excess, shake well and filter.</p>	
	<p><b>Ppt.</b>—Wash well. Dissolve in few drops HCl. Evaporate off excess of acid. Pour into cold water.</p>	<p><b>Filtrate.</b>—Is <i>blue</i> indicates <b>Cu</b>. Add acetic acid in excess. Pass H<sub>2</sub>S for some time. Filter and wash Ppt. Reject filtrate. Boil ppt. in H<sub>2</sub>SO<sub>4</sub> (1 to 6) dilute, filter residue is CuS; reject it. To filtrate add NH<sub>4</sub>OH drop by drop till alkaline, then HCl drop by drop till <i>just</i> acid. Pass H<sub>2</sub>S some time. Yellow Ppt. is CdS and indicates <b>Cd</b>.</p>
	<p>White cloud is BiOCl and indicates <b>Bi</b>.</p>	

acid with hydrochloric acid. This precipitates the arsenic, antimony and tin as sulphides. The mixture is filtered, the filtrate being rejected, and the precipitate removed from the paper after washing, and transferred to a porcelain dish. The transferred precipitate is warmed with hydrochloric acid and a small quantity of potassium chlorate and the mixture boiled until all free chlorine is expelled. If during the operation the fluid becomes very small in bulk, dilute with water. After chlorine is expelled, dilute to three or four times the volume with water and filter. Reject precipitate which should consist only of separated sulphur.

**603.** The filtrate which contains arsenic acid, antimony chloride, and stannic chloride, is introduced into a Marsh apparatus with zinc and dilute sulphuric acid, and the evolved gases passed through a solution of silver nitrate. The gases are allowed to pass through the solution for about fifteen or twenty minutes, and then filtered. The arsenic will be in the filtrate as arsenious acid, and the antimony on the filter paper as a compound of antimony and silver. See **605**.

**604.** Add to the filtrate a small quantity of silver nitrate and then pour carefully on top of this fluid, dilute ammonium hydroxide. A yellow ring at the junction of the two fluids proves *arsenic*.

**605.** The precipitate formed in the silver nitrate solution, after washing with water is boiled with a mixture of hydrochloric and tartaric acids and filtered. The precipitate is rejected, and a current of hydrogen sulphide passed through the filtrate. An orange-red precipitate indicates *antimony*.

**606.** The residue remaining in the generator in which the gases were evolved, is transferred to a porcelain dish and boiled with concentrated hydrochloric acid, the excess of acid being evaporated off, and filtered after diluting with water. The filtrate is tested for *tin* by adding mercuric chloride; and the precipitate after washing with water, dissolved in aqua regia, evaporated to

very small bulk to expel excess of acid, diluted with water, and tested with hydrogen sulphide. An orange-red precipitate indicates *antimony*.

SEPARATION OF THE METALS OF THE FOURTH GROUP. DEPEND-  
ING ON THE SOLUBILITY OF THEIR CHLORIDES  
IN ALCOHOL.

**607.** The group precipitate must be well washed. Prepare some dilute hydrochloric acid (1 of acid to 2 of water), and pour it upon the filter holding the precipitate of the fourth group. The quantity of acid used will depend on the amount of precipitate, but one-third of a test-tube full will usually be sufficient. Hold the funnel over a porcelain dish that is going to be used for the evaporation which follows. If the first passage of the acid through the funnel does not dissolve the whole of the precipitate, return the fluid that has run through into the dish, back to the filter paper again. A second transfer of this kind will usually dissolve the entire precipitate.

**608.** The fluid just obtained is now evaporated to dryness very carefully. To do this the flame under the dish should be a small one, and its point just touch the dish, and, as the fluid evaporates, the dish should be moved around, so that the contents are kept constantly spread over the surface. These precautions are necessary to avoid overheating the solid matter during the evaporation. In fact, the success of the following operations depends upon this first step in the separation of the metals of this group. The greatest possible care is also essential to prevent the sides of the dish that are covered with solid residue from being overheated ; hence a very small flame is used.

**609.** Having driven off all the fluid at a gentle heat, allow the dish to cool thoroughly. Now add to the residue in the dish enough alcohol to make it fluid enough to filter and no more ; in other words keep the bulk of the fluid down. Grind the contents of the dish with a small pestle or flattened end of a glass rod until the alcohol has been very intimately mixed with the residue. Allow the insoluble matter, if any, to settle, pour



off the fluid through a small filter that has been moistened with *alcohol*, not water, into a clean test-tube. Put upon the insoluble matter in the dish another quantity of alcohol equal to twice the first used, grind it with the residue again, and pour it through the same filter paper used previously. The insoluble matter is barium chloride and is treated as follows :

**610.** The residue in the dish or the insoluble matter on the filter paper is treated with water, and the solution filtered into a clean test-tube. This solution is divided into several parts. To one portion add one drop of sulphuric acid ; a heavy, white precipitate which is insoluble in hydrochloric acid indicates the presence of barium. To confirm this test, dip a clean platinum wire into some of the water solution, and heat it in the flame of a Bunsen burner ; a green flame indicates barium. The cleaning of the platinum wire is a very important matter or the color of the flame will be of no value. To clean such a wire, place a few drops of hydrochloric acid in a watch-glass, heat the wire red hot and plunge it into the acid, repeating the operation till the wire will not color the flame when heated in it.

As a still further proof of the presence of barium, the water solution of barium chloride may be tested with a drop or two of potassium dichromate, when a yellow precipitate indicates barium.

**611.** Now take up the alcoholic solution obtained by treating the residue in the dish. To this add sulphuric acid (10 drops will do), shake the mixture well and filter. The acid precipitates strontium and calcium, and the filtrate may be rejected, as it contains nothing that is wanted. Drain the precipitate from the fluid that adheres to it, break a hole through the filter paper with a glass rod, and wash the precipitate into a clean test-tube with as little water as possible. In another test-tube make a solution of ammonium sulphate by taking forty drops of sulphuric acid, four times the volume of water, and adding to this mixture ammonium hydroxide till it smells strongly of the latter. Shake the mixture thoroughly as the ammonium hydroxide is added, and at last add to the mix-

ture one-fourth of its volume more of ammonium hydroxide. The fluid so prepared is now put upon the precipitate obtained with sulphuric acid from the alcoholic solution above. Boil the precipitate with the ammonium sulphate solution for some minutes, taking care not to let it boil over. A gentle boiling is all that is needed. Filter out the insoluble matter.

**612.** The sulphate insoluble in the ammonium sulphate contains strontium if present, and its presence may be detected by heating some of the precipitate, moistened with hydrochloric acid, on a platinum wire in a Bunsen flame. The same care about a clean wire is necessary here as was in the case of barium. It is also necessary to know the color of the flame given by strontium. It is of a bright red tint, and this is brought out by the use of hydrochloric acid on the wire with the precipitate. Calcium gives a flame that is very much like that of strontium, but yellowish-red; a little experience with the two will soon serve to tell the difference.

**613.** In the filtrate from the sulphates boiled with ammonium sulphate, test for calcium by adding ammonium oxalate. A fine, white precipitate indicates the presence of calcium. The only precaution necessary here is that the fluid must be made alkaline with excess of ammonium hydroxide.

The reasons for the various operations for the separation of the metals of the fourth group are as follows:

**614.** The precipitate obtained on adding ammonium carbonate to the filtrate from the third group of metals consists of the carbonates of barium, strontium and calcium. The presence of ammonium chloride in the fluid serves here also, as in the third group, to prevent the precipitation of magnesium carbonate by ammonium carbonate. The fluid also contains ammonium hydroxide in excess, as this is essential to the precipitation of the barium, strontium and calcium as carbonates by ammonium carbonate.

**615.** The precipitate, deprived by washing of any metals of the fifth group, is treated with hydrochloric acid, and the car-

bonates become chlorides of barium, strontium and calcium. These chlorides in solution are obtained in a dry condition by evaporation of the fluid and great care should be taken that they remain as chlorides throughout this operation. The danger is in overheating them as they dry on the sides of the dish. If they are overheated they become oxides of the metals of the fourth group and do not respond to the treatment for their separation.

**616.** The dry chlorides must be allowed to cool or the alcohol will evaporate if it is placed in the hot dish. The treatment with alcohol gives a solution of the strontium and calcium chlorides, which are soluble in it, while the barium chloride remains behind, insoluble. Hence it is important that all the metals should be in the residue as chlorides and not oxides, which latter are not soluble in alcohol.

**617.** The barium chloride is insoluble in alcohol, but it is readily soluble in water. The precipitate obtained with sulphuric acid in the water solution is barium sulphate, which is insoluble in hydrochloric acid. The yellow precipitate obtained with potassium dichromate is barium chromate.

**618.** In the filtrate containing the chlorides of strontium and calcium in alcohol, both metals are precipitated as sulphates when sulphuric acid is added. As this precipitation of the sulphates is complete, the fluid contains nothing except an excess of sulphuric acid, alcohol and water. The precipitated sulphates are boiled with ammonium sulphate and ammonium hydroxide, a mixture that has the power of dissolving out the calcium sulphate, leaving the strontium sulphate insoluble. The calcium sulphate is not very soluble in the ammoniacal mixture; it is therefore not necessary to boil until the solution clears, even if only calcium sulphate is present. Hence a precipitate of calcium sulphate may be obtained which will not entirely dissolve in the ammonium sulphate, and the beginner may think it is strontium sulphate that he has on the filter paper, when it is only some of the calcium sulphate which the ammonium sul-

phate solution has not dissolved because of an insufficiency of the latter. But there is always enough of the calcium sulphate that goes into solution to give the test for calcium if that metal is present.

**619.** The filtrate from the insoluble sulphates, which must be alkaline, is mixed with ammonium oxalate, which gives a precipitate of calcium oxalate if calcium is present ; a very characteristic test for this metal. The precipitate is fine and white. It is insoluble in acetic acid, but dissolves in hydrochloric acid.

**620.** In testing the precipitate of sulphate upon the filter paper, the only thing to remember is that it may contain both calcium sulphate and strontium sulphate, unless the first is present in very moderate quantities, and this calcium sulphate gives an orange-red flame when heated on the platinum wire. But a little experience will soon show the difference between the two colors. Special tests for strontium are also made in cases of doubt.

The operations described above are tabulated in the following scheme :

## (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> Group.

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Dissolve in HCl (1 in 3). evaporate to dryness, *don't overheat*. Allow to cool, add alcohol, grind up with pestle, pour off, and repeat treatment with alcohol, filter and wash with alcohol. *Moisten filter paper with alcohol, not water.*

**Insoluble**—Dissolve in water and add H<sub>2</sub>SO<sub>4</sub>. A white ppt. is BaSO<sub>4</sub> and indicates **Ba**.  
Also test in flame, and with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. A yellow ppt. proves **Ba**.

**Filtrate**.—Add H<sub>2</sub>SO<sub>4</sub>, shake well, filter and wash. *Reject filtrate.* **Ppt.**—Boil with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>+NH<sub>4</sub>OH for some minutes and filter.

<p><b>Ppt.</b>—Test on Pt wire in Bunsen flame. Red flame indicates <b>Sr</b>.</p>	<p><b>Filtrate</b>.—Add [(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]. Fine white ppt. indicates <b>Ca</b>.</p>
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## DETECTION OF THE ACID RADICALS OR ACIDS.

The method of procedure for their detection is as follows :

**621.** *If the material is a fluid*, evaporate half of it very carefully to dryness, avoiding overheating. The solid residue is submitted to the following tests, using a small and *fresh portion* for each experiment. *If the material is a solid* it may be used at once.

**622.** A.—Heat on charcoal before the blowpipe.

The substance *deflagrates* : indication of the presence of nitrates or chlorates or both.

The substance *carbonizes* : indication of an organic acid.

**623.** B.—If the substance deflagrates on charcoal, put a little of it upon the surface of a few drops of sulphuric acid in a watch-glass. A yellowish-brown color and a chlorous odor indicate *chlorates*.

**624.** C.—If the substance deflagrates on charcoal, put a little of it into a test-tube, add sulphuric acid, and then pour upon the top of the mixture a strong solution of ferrous sulphate. A dark brown ring at the junction of the two fluids indicates *nitrates*.

**625.** In the two last tests the color due to the presence of chlorates or nitrates may be completely masked by a deep brown color from iodides, or an orange-red color from bromides, if either of them are present. To test for nitrates or chlorates in presence of iodides or bromides, the following methods are used :

**626.** For *nitrates*. If ammonium salts have been found while testing for the metals, boil some of the original material (solution or solid) with excess of sodium carbonate until it is almost reduced to dryness, to expel ammonia. To this fluid now add a little water, a few drops of sulphuric acid until it is acid to test

paper, a drop or two of copper sulphate and then a piece of sheet zinc. Allow the action to go on for five minutes ; and if there is not a brisk action, add a few more drops of acid. This will convert the nitrates into ammonium compounds, and if sodium hydroxide in excess is added to some of the mixture poured into another tube, the odor of ammonia gas will be noted on warming. This is an indication of the presence of nitrates.

**627.** For *chlorates*. To a solution of the original material add nitric acid in excess and then silver nitrate until it will produce no more precipitate. This will precipitate all chlorides, bromides, iodides, cyanides, ferrocyanides, ferricyanides and sulphides. Filter out the precipitate and reject it. To the filtrate add sodium carbonate in slight excess, boil and filter. This will precipitate any silver that may be present, and the filtrate will contain the chlorates if they are present. Add excess of sulphuric acid to the filtrate, then a drop or two of copper sulphate and a piece of sheet zinc. Allow the action to go on for five minutes, and if it is not brisk, add a few more drops of sulphuric acid. Pour off the fluid from the zinc, add to it a few drops of nitric acid and then silver nitrate. A white precipitate, soluble in excess of ammonium hydroxide, indicates the presence of chlorates. The chlorates do not give a precipitate with silver nitrate, but the zinc and sulphuric acid reduce them to chlorides, which give a precipitate.

**628.** D.—Put a little of the substance into a test-tube and pour upon it dilute hydrochloric acid (1 in 3). If a gas is given off, note its odor.

If it has the odor of hydrogen sulphide, *sulphides* are present.

**629.** If it has the odor of burning sulphur, it indicates the presence of *sulphites*.

**630.** If it has the odor of hydrocyanic acid, *cyanides* are present.

**631.** If it has no odor, it is probably carbon dioxide. In this case take some clear lime water and pour the *gas* from the test-tube into it, shaking the lime water. The formation of a white precipitate indicates the presence of *carbonates*.

N. B. Always apply the lime water test, even when an odor of other acids is obtained.

**632.** There are several precautions necessary in applying the tests under D. In the first place, the dilute hydrochloric acid must be free from odor before it is put upon the substance to be tested. To secure this freedom from odor, the strong acid is mixed with the water in a test tube, and the mixture is well shaken, until, on applying the nose, no odor is detected in the tube. This is especially necessary in the detection of sulphites and cyanides. The second precaution to be taken is, in testing for carbon dioxide, that none of the acid fluid falls into the lime water when the gas is poured into the tube.

**633.** E.—Mix some of the substance to a paste with sulphuric acid in a watch-glass, and test a portion of the mixture in a blowpipe flame on a platinum wire which has been moistened with strong glycerin. A flame having a leaf-green border indicates *borates*. The test is very delicate, but the duration of the color is very short. In presence of copper and barium, apply this test to some of the solution, see **648**.

**634.** F.—Put some of the substance into a test-tube and add a few drops of alcohol to it, then pour into the mixture a few drops of sulphuric acid, warm it, and note the odor. An odor of acetic ether indicates *acetates*. If acetates are present, a carbonizing of the substance will have been noted in **622**.

**635.** G.—Mix the substance with sulphuric acid in a watch-glass and set it aside for ten minutes. Wash out the mixture with water and note if the surface of the glass has been roughened where the mixture was in contact



with it. The effect is best seen by drying the glass and then breathing upon it. Such roughening indicates the presence of *fluorides*.

Care should be taken that the glass is not rough before testing in it.

- 636.** H.—Mix the substance with enough nitric acid to turn blue litmus paper red and then dry the mixture. To the residue add nitric acid again, warm it gently and add water to this mixture; if there is any matter that remains insoluble in water after stirring it, it is silica, and indicates the presence of *silicates*. Test the insoluble matter in the sodium metaphosphate bead.

**637.** Add to the *solution* of the substance (or boil the *solid* with) a solution of sodium carbonate (1 in 5) until it is decidedly alkaline to red litmus paper. Boil for some minutes and filter the fluid while it is hot. Test the precipitate, or insoluble, if any, for silicates, fluorides and phosphates. Use the solution for the following tests, taking a *separate* quantity for each.

- 638.** *a.*—To the solution add nitric acid until it is acid to test paper. Then add silver nitrate. A white curdy precipitate indicates the presence of either chlorides, bromides, iodides, cyanides, ferrocyanides, ferricyanides or sulphides, or all of them. No precipitate with silver nitrate indicates the absence of these radicals.

Having added an excess of silver nitrate to the acid solution, to be sure that no more precipitate is obtainable, shake the mixture well and allow the precipitate to settle. Pour off the fluid and reject it. Shake the precipitate with a little water, allow it to settle and again pour off the fluid and reject it. To the washed precipitate add ammonium hydroxide, shake well and filter.

The insoluble matter may contain silver iodide, bromide, ferrocyanide, or sulphide, or all of these.

The solution may contain silver chloride, cyanide or ferricyanide, or all of these. Now add nitric acid

to the solution until it reddens blue litmus paper, when a precipitate of the last three silver compounds will be obtained, or of any one of them, if they are present. If a precipitate is not obtained, they are not present.

If the precipitate is entirely soluble in ammonium hydroxide, one or all of the last three silver compounds may be present.

In case a portion of the silver precipitate is soluble and another portion insoluble in ammonium hydroxide, all of them may be present, and all the tests given below must be made.

- 639.** *b.*—Add hydrochloric acid until just acid to litmus paper. In a separate test-tube, generate a little chlorine gas, with hydrochloric acid and potassium chlorate. Pour *a little* of this gas into the acid fluid previously prepared, and shake the mixture. A dark brown fluid, a few drops of which give a deep blue color with cold starch paste, indicates the presence of *iodides*.
- 640.** *c.*—If iodides have been found in *b*, add carbon disulphide, and then hydrochloric acid in excess. To this fluid add sodium hypochlorite, drop by drop, shaking the mixture, and keeping it acid. In presence of iodides, the carbon disulphide is first colored violet by separated iodine, and, as the hypochlorite is added, this color is bleached out, or it gives place to a yellow-brown color of separated bromine, which indicates *bromides*. Extreme care is necessary to avoid adding too much hypochlorite, but the test is a very good one.
- 641.** *d.*—If the precipitate in *a* is partly or entirely soluble in ammonium hydroxide, chlorides and cyanides may be present. To determine if chlorides are present (cyanides are found in **630**), wash and dry some of the precipitate soluble in ammonium hydroxide (repre-

precipitating it with nitric acid, see **638**), and melt it in a small porcelain dish. Silver cyanide is decomposed, while the chloride is not affected. After cooling, add a little water to the dish, and place in contact with the melted precipitate a piece of zinc, adding sulphuric acid until a brisk action takes place. This converts the silver chloride into silver, and zinc chloride is formed in solution. After a few minutes, filter, add nitric acid to the filtrate, and then silver nitrate. A white precipitate, soluble in ammonium hydroxide, indicates *chlorides*.

**642. e.**—Add excess of hydrochloric acid and then ferrous sulphate; a blue precipitate indicates the presence of *ferricyanides*.

**643. f.**—Add excess of hydrochloric acid and then ferric chloride; a blue precipitate indicates *ferrocyanides*.

N.B.—No test is required here to determine the presence of cyanides; these should have been found already in **630**.

**644. g.**—Add hydrochloric acid in excess and boil (solution should be acid after boiling), and then barium chloride; a white precipitate indicates the presence of *sulphates*.

**645. h.**—If the solution **637** is yellow, add excess of acetic acid and then lead acetate; a yellow precipitate, soluble in sodium hydroxide, indicates *chromates*.

If the solution is not yellow, chromates are absent.

**646. i.**—Add nitric acid in excess and boil the mixture. Add a few drops of this mixture to molybdic solution and warm; a yellow precipitate indicates *phosphates*.

**647. N. B.**—If arsenic has been found when testing for the metals, a test must be made to determine if arsenic acid is present. In this case add excess of nitric acid to the solution **637** and then silver nitrate until it gives no more precipitate. Filter out this precipitate, if any, and reject it. To the filtrate add

ammonium hydroxide in such a manner that it floats upon the surface of the fluid. A reddish-brown precipitate at the junction of the two fluids indicates *arsenates*. A yellow precipitate here indicates *arsenites*. If arsenates are found, the yellow precipitate (646) may contain this acid radical. In this case add to solution 637 an excess of hydrochloric acid, then heat to near the boiling point and pass hydrogen sulphide. Continue passing the gas and warming the solution for five minutes; this will precipitate the arsenic of both arsenates and arsenites. Filter out the precipitate, add nitric acid, and boil, to decompose hydrogen sulphide. Filter if necessary, add a few drops of the filtrate to molybdic solution and warm the mixture; a fine yellow precipitate now indicates the presence of *phosphates*.

648. *j*.—If copper or barium is present, the solution 637 must be tested for borates. For this purpose evaporate some of it nearly to dryness, add sulphuric acid to form a paste and then test with glycerin in the blow-pipe flame; a leaf-green border to the flame indicates *borates*. See 633.

649. *k*.—Add hydrochloric acid in excess, and boil (the fluid should be acid after boiling), then add dilute sodium hydroxide (1 of solution and 4 of water) drop by drop until the fluid is just alkaline. To this add calcium chloride; a white precipitate indicates oxalates or tartrates, or both.

Filter out the precipitate and test the filtrate with more calcium chloride to see if precipitation is complete. The filtrate freed from oxalates or tartrates is rejected.

The precipitate is washed with acetic acid on the filter and the solution passing through is allowed to run into a test-tube. If the substance contains potassium, a crystalline precipitate of acid tartrate of potassium may separate in the acetic acid filtrate; this is allowed to remain. The acid is passed through the filter several times to see if all the precipitate will dis-

solve. If it all dissolves, only tartrates are present, and on adding dilute sodium hydroxide (see above) to the acetic acid fluid until it is just neutral, calcium tartrate is precipitated again. This latter should be filtered out, partially dried on the filter paper and then heated on platinum foil. An odor of burning grapes indicates *tartrates*. If tartrates are present, the substance carbonizes on charcoal (see 622.) The precipitate, insoluble in acetic acid, should be dissolved in hydrochloric acid, the solution mixed with an excess of ammonium hydroxide, which again gives a precipitate of calcium oxalate, insoluble in acetic acid, indicating the presence of *oxalates*.

650. *L.*—Add hydrochloric acid until the fluid is just acid to litmus paper. Now boil the mixture for some time and test again with litmus paper. If the paper turns red, add dilute sodium hydroxide (1 of solution, 4 of water), drop by drop, until the fluid is neutral, that is, does not change the color of the test paper. Add some of this solution to a test-tube full of lime water. If a precipitate is formed, filter it out (it is probably calcium oxalate or tartrate), and boil the filtrate; a precipitate indicates *citrates*. If citrates are present the substance will carbonize on charcoal (see 622.).

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